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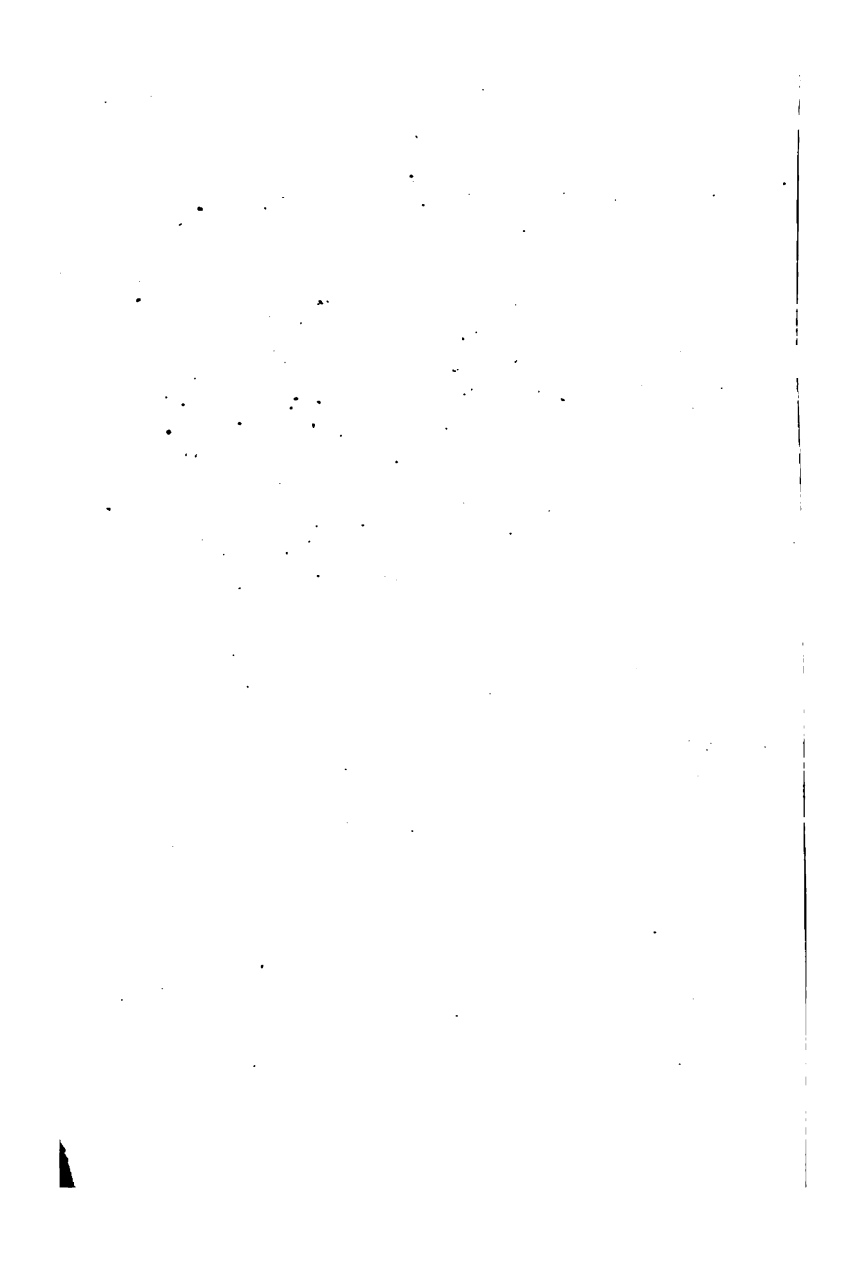
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REYNOLDS'S
EXPERIMENTAL CHEMISTRY
PART. II.
NON-METALS.







EXPERIMENTAL CHEMISTRY.

PART II.

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EXPERIMENTAL CHEMISTRY

FOR

JUNIOR STUDENTS.

BY

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PART II.—NON-METALS

(with an Appendix on Systematic Testing for Acids).

THIRD EDITION.

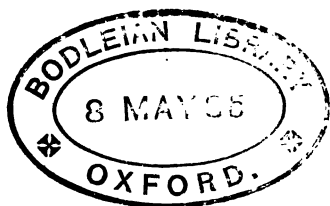
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EXPERIMENTAL CHEMISTRY

FOR
JUNIOR STUDENTS.

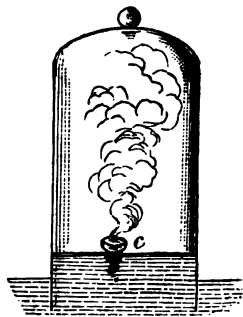
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CHAPTER XIII.

EXPERIMENTS WITH AIR AND NITROGEN.

Experiment 81.—Cut a piece of phosphorus about the size of a pea, dry it by very gentle pressure between folds of blotting-paper, and place it in the small porcelain capsule *c*, fig. 51, which floats on the water in the pneumatic trough. Fire the phosphorus by the touch of a hot wire, and immediately invert over it the bell-jar, which is at first full of air. The mouth of this jar must be under the surface of the water so as to completely inclose the gas it contains. Bubbles of air escape at first, owing

FIG. 51.



to expansion by the heat, but soon contraction takes place and the water rises in the jar. The white fumes produced during the combustion of the phosphorus are the same in composition as those formed in Experiment 60, *i.e.* P_2O_5 , and we already know that they dissolve in water and form phosphoric acid ; thus the oxygen of the confined mass of air is removed in the form of solid oxide of phosphorus, and the latter is washed away by the water ; the gas in the jar therefore contracts in volume. Now it is obvious that if air consisted only of oxygen, and we used sufficient phosphorus in our experiment, all the gas would disappear and water would completely fill the jar ; but, as a matter of fact, the phosphorus soon ceases to burn, and then, on allowing the jar to stand over water until the white fumes disappear, we find that a considerable volume of colourless gas remains behind.

Now transfer this gas to smaller tubes in the manner directed in Experiment 17, and make the following observations :—

a. A tube full of gas when turned up is found to be free from smell, if it has been washed thoroughly from all fumes.

b. A burning taper plunged into another tube full of the gas is immediately extinguished.

c. A little 'lime-water' shaken into another jar of gas is not rendered milky, unlike the result obtained with the carbon dioxide gas formed in Experiment 58.

Therefore air from which oxygen has been removed is colourless and inodorous ; it is incom-
bustible, does not support the combustion of a taper,

and does not render lime-water turbid. This gas wholly consists of another elementary form of matter, which is called

NITROGEN ¹—*Symbol* N^v = 14. 1 Vol weighs 14 c.grs.
Molecular weight = 28.

Nitrogen does not support animal life, and is sometimes called *azote*,² in consequence. It is very slightly soluble in water ; 1 c.c. of water dissolves only 0.01478 c.c. at 15° C.

Free nitrogen is one of the most indifferent gases we are acquainted with in its chemical relations, and thus contrasts strongly with the energetic oxygen. Pure atmospheric air, then, consists of these two dissimilar gases. We next have to determine the proportions in which these bodies are present in air. The rough experiment just made can give us an approximate result, for when we measure the maximum height to which the water rises in the jar after removal of the oxygen by phosphorus, we find that about *one-fifth* of the gas has disappeared. A similar, but much slower and more accurate, experiment may be made in the following way :—

Experiment 82.—Fill the graduated tube *a*, fig. 52, with 100 c.cs. of air, taking care that the volume is measured when the water stands at the same height within the tube and without in the beaker. Now fix the tube in its support, and pass high up into the confined air a small stick of phosphorus attached to a stout copper wire. Secure the wire in its place and

¹ From νιτρον, nitre, and γενναω, I generate.

² α, privative, and ζωη.

leave the whole for twenty-four hours. The phosphorus slowly combines with and removes the oxygen, and leaves only nitrogen. In order to measure the

FIG. 52.

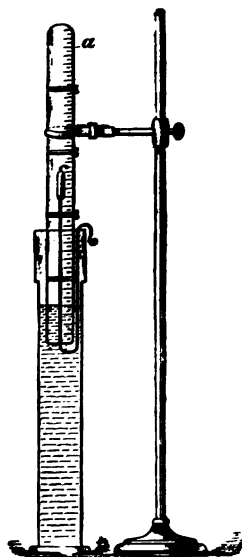


FIG. 53.



latter, withdraw the phosphorus, adjust the water-level again, and read the graduation. If the temperature and pressure are unchanged, the residual nitrogen

in the tube will measure slightly more than 79 c.cs. ; the difference, or oxygen absorbed, is, therefore, nearly 21 c.cs.

Or another, and very rapid, method of analysis by absorption may be used, which is founded upon the fact that a mixture of caustic potash and pyrogallic acid, or pyrogallol, absorbs free oxygen gas with great avidity.

Experiment 83.—Take a cylindrical tube, 1 meter long and about 16 millimeters diameter. One end is sealed, the other is closed by an india-rubber cork, through which the tube of the little bulb apparatus, fig. 53, passes. Divide the tube from the end to the cork into *six* equal parts, marking off the parts by thin elastic rings slipped over the tube. Now remove the cork and fill up to the first ring *a* with strong caustic potash solution, replace the cork, close the stopcock *s*, and fill the bulb *b* with a strong solution of pyrogallic acid ; then open the tap *s* and allow a few drops to fall into the tube (but do not let air escape). Again close *s*, press the thumb over *o*, and invert the apparatus so as to mix the caustic potash with the small quantity of pyrogallic solution, and thus to expose the gas to the action of the mixture. Bring the tube back to the position in which *b* is uppermost, remove the thumb from *o*, and cautiously open *s* ; the liquid rapidly runs in from the bulb now, as absorption has taken place. Again close *s* and proceed as before. Repeat these operations until on opening *s* only a drop or two of liquid passes into the tube, showing that all the oxygen has been absorbed. Now close *s*, fill the bulb completely with water, close *a*

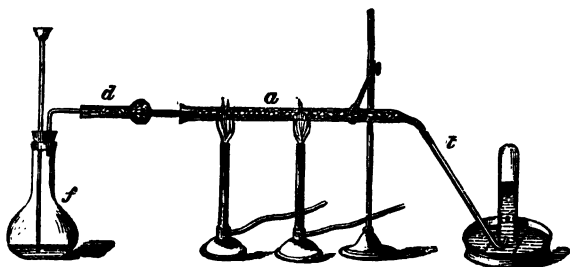
with the thumb, and invert in a tall vessel of water. On opening *s* the heavier dark liquid flows out, and is soon replaced by pure water. Adjust the liquid to the same level within and without by depressing the tube to the requisite extent. The water should then stand above the *second* ring, or, on a graduated tube, at 20.9 divisions out of 100 of air.

Experiment 84.—Fill the eudiometer used in Experiment 23 with *water* in the large pneumatic trough, and allow about one-third the water to be displaced by air; adjust the water to the same level within and without the tube, and note the volume. Now pass in half the volume of pure hydrogen gas, level again, and read the total volume. The hydrogen can be easily obtained from the apparatus used in Experiment 68 if dilute sulphuric acid be employed in it, and the wire *w* be connected with the zinc end of the battery; gas should not be collected in the eudiometer until sufficient has been separated by electrolysis to expel all traces of air from the apparatus. The tube instead of passing into the bottle, as shown, should, of course, dip under the surface of the water in the pneumatic trough. Press the mouth of the eudiometer on an india-rubber pad placed between it and the bottom of the trough; now grasp the tube, hold it firmly against the pad, and pass a spark between the internal wires. After explosion relax the pressure on the tube and allow water to enter; adjust levels again and read. *One-third* of the total contraction observed represents oxygen present in the air, for we already know from Experiment 23 that two volumes of hydrogen and one volume of oxygen unite

to form water, which latter condenses at ordinary temperature.

If, in a particular experiment, 100 parts of air are mixed with 50 of pure hydrogen, and after explosion the residual gas measures 87·3 parts, the pressure and temperature being the same at the beginning and end of the operation, we can calculate the composition of air by volume thus :—The contraction after explosion is $150 - 87\cdot3 = 62\cdot7$ parts. Then $\frac{62\cdot7}{3} = 20\cdot9$ — the

FIG. 54.



proportion of oxygen gas in the original 100 parts by volume of pure air. The difference, or $100 - 20\cdot9 = 79\cdot1$, is the percentage of nitrogen gas.

Experiment 85.—Fill the tube of hard glass, *a*, fig. 54, with bright copper turnings, support it as shown, and heat with a large gas or spirit flame; connect the end by means of an india-rubber tube with a glass delivery tube, *z*, which latter dip under the water in the pneumatic trough. The flask *f* should only contain water enough to cover the end of the

funnel tube. Now apply heat to the tube containing the copper turnings, and when a red heat is reached pour water into the funnel tube of the flask ; air is thus made to pass over the calcium chloride in *d*, and then over the hot copper, which latter combines with the oxygen and forms dark copper oxide, CuO , while nitrogen gas bubbles from the delivery tube through the water in the trough, and should be collected in tubes and tested in the manner already described.

This experiment illustrates the principle of the method adopted by Dumas and Boussingault in their precise determination of the composition of air by weight. They caused pure dry air to pass over red-hot copper contained in a glass tube, and thence into an exhausted glass globe ; each portion of the apparatus was accurately weighed before an experiment. The tube and globe were separately weighed after an experiment. The former gained in weight, owing to the combination of the copper and oxygen, and the gain of the globe was due to nitrogen ; the sum of these quantities was the weight of air operated upon. The mean of a number of laborious experiments of this kind, in which every possible precaution against error was adopted, gave the following results, which, for convenience, we compare with those of the volumetric analysis of air already described :—

Percentage of	By weight	By volume
Nitrogen . . .	76.995 .	79.1
Oxygen	23.005 .	20.9

If nitrogen and oxygen were of the same specific

gravity, the percentage composition of air by weight and volume would be the same; but we have already seen that the specific gravity of $N=14$ and of $O=16$ ($H=1$); hence as oxygen is, volume for volume, a little heavier than nitrogen, it follows that one volume of oxygen must weigh *more* than one-fifth of the total weight of five volumes of air, although oxygen forms but one-fifth by volume of the gas.

The specific gravity of pure dry air is 14.47 ($H=1$). Therefore, one *Vol* (i.e. 112 c.cs.) weighs 14.47 c.grs.

Atmospheric air is *nearly* constant in composition. The results of numerous precise analyses of pure air, collected at various and widely-separated points of the earth's surface, and at considerable heights above sea-level during balloon and mountain ascents, prove that the variations in the proportion of oxygen are well within one-fifth per cent. by volume. In tropical countries, however, the oxygen has been observed to drop suddenly as low as 20.3 per cent., owing to some hitherto undetermined cause.

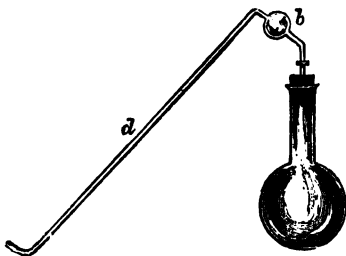
If *pure* air were a definite chemical compound of nitrogen and oxygen it should be absolutely constant in composition, and we know that it is not quite constant, therefore *it is not a definite chemical compound*. Again, oxygen and nitrogen are not present in simple atomic proportions in pure air, the ratio being 3.9 atoms of nitrogen to 1 of oxygen. If the conclusion just stated be true, a mere mixture of the two gases in the proportions indicated by analysis ought to possess all the properties of air. To test this, make—

Experiment 86.—Fill a gas jar with water and invert it in the pneumatic trough ; introduce as much nitrogen gas (prepared as in Experiment 81) as will displace four-fifths of the water, and as much oxygen (prepared as in Experiment 57) as will completely fill the jar. This is an evident mixture of the two gases, and no heat is developed, nor can we find that any other physical change accompanies the mixture—nothing occurs to indicate that any chemical action whatever has taken place between the two gases. Now remove the jar in the usual way, invert it, and plunge a match with glowing tip into the jar ; it is not rekindled as it would be in pure oxygen. Plunge a burning taper into the gas, and it continues to burn as it did in air. In fact, in all respects this mixture of the two gases acts just like atmospheric air, and all the characters of the latter are those of oxygen much diluted with just such an indifferent body as we know nitrogen to be. We thus have *synthetic* evidence in favour of the mixture view.

Experiment 87.—Take a flask capable of holding rather more than one liter, fit it with an india-rubber cork carrying the bulb tube *b*, fig. 55, but the short tube of the latter must not pass quite through the cork. *Completely* fill the flask with clean and fresh rain water, and the bulb tube also ; insert the cork carrying the latter in the neck of the flask in such a way as to have the flask and tube quite full of water. Let the delivery tube, *d*, dip under some of the same water contained in a small trough, and invert over it a test-tube filled with water. Apply heat to the flask

and gradually raise the water to the boiling point; bubbles of gas will be evolved all the time and collect in the bulb *b*; this is air previously dissolved by the water from the atmosphere. When the boiling point is reached, the steam generated pushes the air through the tube and into the test-tube placed to receive it. If the boiling be continued for some time, all the air originally dissolved in the water can be expelled and collected with little loss in the test-tube.

FIG. 55.



One liter of water fully charged with air at 15° C. should afford 17.95 c.cs., but this volume is rarely obtained.¹ If the test-tube be removed from the water, then inverted, and a burning match be now plunged into the air extracted from the water, the combustion of the wood will be much more active for a few seconds than in air. We are thus led to suspect that air extracted from water contains more oxygen than ordinary air, and when analysed by any

¹ The residual water is quite flat and insipid.

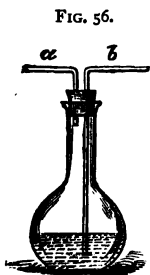
of the methods already given, it is found to contain in 100 volumes :—

Nitrogen	65'
Oxygen	35'
							<hr/> 100'

That is to say, water dissolves more oxygen, in proportion, out of air than nitrogen, because the former is more soluble. This fact confirms the conclusion that *air is a mere mechanical mixture of the two gases*, for if it was a chemical compound the air extracted from water should have the same composition as that of the atmosphere.

Small though the proportion of air dissolved in water is, it makes all the difference between life and death to fish, as the oxygen they can withdraw from

water by their respiratory organs—the gills—is essential to their existence. Hence it is necessary to secure the due aëration of water in *aquaria*, either by frequently changing or by making a number of fine streams of air-bubbles pass through the liquid.



Experiment 88.—Arrange a bottle as shown in fig. 56. Put some lime-water into it, and insert the cork carrying the two tubes *a* and *b*. Apply the mouth to *a* and *inhale* or suck in air through it into the lungs; the air enters through *b* and bubbles through the lime-water, but it does not render the liquid turbid in its passage. Now apply the lips to *b*

and *exhale* air from the lungs through the tube ; the air from the lungs bubbles through the lime-water, and the latter soon becomes turbid. We have already learned from Experiment 58 that the lime-water acts 'as a detector' of carbon dioxide or carbonic acid in a gas ; therefore the expired air differs from that inspired by containing much carbonic acid gas.

Experiment 89.—Expired air is analysed by collecting it in a graduated tube¹ over mercury. A few drops of strong solution of caustic potash are then passed up through the mercury into the confined gas from a curved pipette, as shown in fig. 57. The carbon dioxide is quickly absorbed by the alkali in the production of potassium carbonate, thus :—

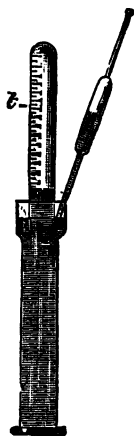
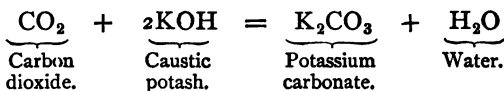


FIG. 57.



The contraction in volume observed, after adjusting for level, gives the proportion of carbon dioxide.

¹ The graduated tube is first filled with mercury and then inverted in the same liquid. A tube of glass, curved at one end like the pipette in fig. 57, is used to convey the air from the lungs into *t*. The first portions of air expelled from the mouth must be allowed to escape, and the later only collected, by forcing it through the mercury into *t*.

If a small quantity of strong solution of pyrogallie acid be now introduced, a further contraction takes place, due, as in Experiment 83, to absorption of oxygen; this is measured, and the residual gas is nitrogen, whose volume is then determined. In this way the composition of a sample of air expired by a man was found to be, in 100 volumes—

Nitrogen	.	.	.	79.58
Oxygen	.	.	.	16.04
Carbon dioxide	.	.	.	4.38
				<hr/> 100.00

Therefore, during animal respiration, between 4 and 5 per cent. of oxygen is consumed in the process, evidently in the combustion of carbonised material, and a nearly equal volume of carbon dioxide is evolved. An adult man thus expires about 450 liters of CO_2 in twenty-four hours.

Experiment 90.—Pour 30 or 40 c.cs. of lime-water into a wide-mouthed bottle; now plunge a burning taper or candle into the air in the bottle and let it burn for a short time; then remove the taper, close the mouth with the hand, and shake. The lime-water becomes very turbid, therefore carbon dioxide was produced during the combustion of the taper.

A similar experiment may be made with the flame of a small petroleum lamp or of coal-gas, or with a piece of red-hot coal. In all these cases carbon dioxide is a product of the combustion, and the detection of this particular product proves the presence of the element carbon in the body burned.

We have thus detected several sources of con-

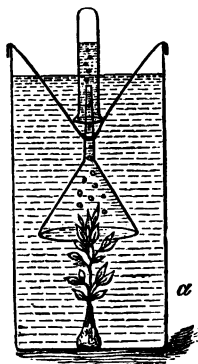
tamination of air by carbon dioxide gas, and since most of these causes have been and are constantly in operation the atmosphere should have long since become hopelessly impure and even poisonous to man. We know that it is not ; therefore some great natural process of purification must be constantly at work. The next experiment will help us to understand the nature of this process.

Experiment 91.—We take for our purpose one or other of the following plants—the common *Anacharis*, *Potamogeton natans*, to be found in our ditches and rivers, *Elodea canadensis*, *Ceratophyllum*, *Hettonia*, *Spirogyra*, or any whose leaves have large stomata.

Nearly fill a tall cylinder (a, fig. 58) with water saturated with carbon dioxide by the method described later on. Attach a portion of the plant, with as many fresh leaves as possible, to a piece of stone, in order to sink it in the water in the cylinder, and to retain it in the position shown.

Next suspend over the plant an inverted funnel, and secure it in position by means of wire stays. Fill a test-tube with water, invert and slip the mouth over the tube of the funnel, as shown. Observe now that no change takes place in a feeble light, but expose the whole arrangement to bright sunshine for some hours and bubbles of gas will be evolved, and

FIG. 58.



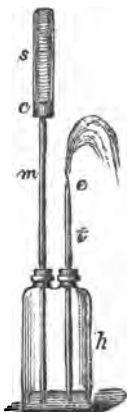
will rise through the funnel and collect in the test tube. When a sufficient quantity has been collected, remove the tube in the usual way, invert it, and plunge into the gas a match with a glowing tip ; note that it is rekindled. The gas can be easily identified as pure oxygen thus evolved from the plant. A careful examination of this process of separation of oxygen has shown that the latter is a product of the decomposition of CO_2 in the green or *chlorophyll* cells of the leaves ; in these cells the carbon is fixed and employed in the production of various carbonised bodies, starch, woody fibre, &c., while any oxygen not required for similar purposes in the plant-organism is returned to the atmosphere in the gaseous form, as we have seen.¹ We learn, thus, that the carbon dioxide which issues from the lungs of a man or other animal, from the burning candle, the factory fire, and many other sources, and that would, if allowed to accumulate, soon render the atmosphere deadly to the higher animals, is rapidly decomposed by vegetation under the influence of the solar rays. Thus man is saved from slow poisoning by the depurating action of vegetation on impure air, and this action is, moreover, the chief cause of the nearly constant composition of

¹ In addition to this decomposition of carbon dioxide, which is only effected in the chlorophyll cells under the influence of light—and chiefly of the yellow rays—a process of *respiration* analogous to that of animals takes place in all parts of the plant, and is not dependent on the action of light ; but this absorption of oxygen and evolution of carbon dioxide is so very feeble that the loss of carbon involved is insignificant when compared with the enormous gain of carbon by decomposition of its dioxide in the chlorophyll cells.

the air, aided as it is by the action of atmospheric currents arising from alterations of temperature, and the operation of a curious physical law in virtue of which the constituents of a gaseous mixture tend to diffuse or distribute themselves equally throughout the mass. This principle can be easily illustrated by the following experiment.

Experiment 92.—Fit the double-necked bottle *h* as shown in fig. 59. The tube *t* passes through the cork nearly to the bottom of the bottle, where it dips just under the surface of some water coloured with litmus or cochineal; this tube is drawn out to a rather fine jet at the end *e*. Both corks are best of india-rubber; through the second passes the long tube *m*; this, like *t*, should just dip under the surface of the water in *h*. The end outside the bottle passes airtight through the cork *c*, which closes the porous earthenware cell *s*. The latter is one of the small porous cells used for galvanic batteries, and should be new and clean. All the corks, if not of rubber and very tight, must be coated with paraffin. Having prepared the apparatus, fill a rather large jar with hydrogen, and bring it mouth downwards over *s*. Almost immediately gas bubbles from *m* through the liquid in the bottle, and as it has no exit it is confined in *h* and exerts considerable pressure upon the surface of the coloured water, which latter is, in consequence, driven up through *t* and issues from *e*, forming a temporary fountain. On

FIG. 59.



withdrawing the jar the reverse action takes place—air enters through *t*, and the liquid rises in *m*.

The reason for the accumulation of gas within the apparatus at first, and consequent increase of pressure, is that the hydrogen rapidly diffuses itself through the air in the cell and *vice versa*, while the porous cell walls do not oppose material obstacles to this process of diffusion, though sufficient to intercept mere currents. But hydrogen gas, being so much lighter than air (in the ratio of 1 to 14.47), rushes through the pores at a higher rate than the heavier air can pass in the opposite direction—consequently gas accumulates in the cell, and the evidence of this is the increased pressure within the apparatus, which suffices to raise a column of liquid to a considerable height. If oxygen were present at first in the cell, the pressure would be still higher, owing to the greater specific gravity of that gas. The law regulating this diffusion of gases is called 'Graham's law,' as it was discovered by the late Professor Graham, the last scientific Master of the British Mint, and its statement is that *the diffusion rates of two masses of gas in contact are inversely proportional to the square roots of their specific gravities*. Thus, comparing hydrogen and oxygen, the specific gravity of the latter is 16, and the square root of 16 is 4—therefore, according to the law, four times as much hydrogen as oxygen will pass through the cell wall in a given time.

In the case of air the two constituents do not diffuse out into the external hydrogen at the same rate, the heavier oxygen passing out in the above proportion, and the somewhat lighter nitrogen at a higher rate.

IMPURITIES IN AIR.

The impurities commonly met with in air are the floating solid particles—the ‘motes in the sun-beam’ beautifully seen when a beam of sunlight passes through the air—and the gaseous or vaporous bodies we should expect to find, viz., carbon dioxide, water, ammonia, and ozone; while we occasionally meet with carbon monoxide, marsh gas, and other hydrocarbides, sulphur dioxide, sulphuretted hydrogen, oxides of nitrogen, chlorine, and organic emanations from the skins and lungs of men and other animals.

Experiment 93.—Expose in a dish a quantity of lime water to the air of some open space for a few hours; the water will soon be covered with a white pellicle, owing to the formation of chalk arising from the action of the carbon dioxide, always present in ordinary air, upon the lime in the water (see Experiment 58).

The usual proportion of CO_2 in good fresh air is from 0.033 to 0.04 per cent., i.e. 3 to 4 parts in 10,000, but the air of confined and ill-ventilated spaces is often much less pure, as it is rapidly altered by animal respiration and burning illuminating materials.

An adult man expires about sixteen cubic feet of air per hour, and about $\frac{1}{30}$ th of this is carbon dioxide. A single gas-jet which consumes three cubic feet of coal gas per hour (equal to about 150 grams of oil or fat) uses up more air than two men.

When the proportion of carbon dioxide reaches 0.09 to 0.1 per cent., the air is close and ‘fusty’ to the senses, and is unwholesome. The late Dr. Parkes

held, and we think rightly, that air should be considered unwholesome for human beings when the carbon dioxide present exceeds 0.06 per cent., or 6 volumes in 10,000, the carbon dioxide being in this case taken as a measure of the general purity of the atmosphere.¹ Good ventilation aims at keeping the atmosphere of a room well under this standard, and for this purpose 3,000 cubic feet of fresh air must be introduced per head every hour, and about twice this volume of fresh air per hour for each gas-burner that hourly consumes three cubic feet of coal gas, unless the products of combustion are removed by special means.²

Experiment 94.—Take two plates ; expose to the air on one some lumps of calcium chloride, and on the other some common pearlash—impure potassium carbonate. After a time both substances will be found in a moist condition, having absorbed aqueous vapour from the atmosphere and dissolved in it, or *deliquesced* ; if exposed long enough each will become completely liquid, and a strong solution of calcium chloride be formed in one case and of potassium carbonate in the other. Both substances are spoken of as *hygroscopic*, or moisture-imbibing bodies, and thus serve to prove the presence of water in the air.

¹ Two methods will be found in Chapter XX. for the estimation of CO_2 in air.

² The amount of air-space required for healthy adults in a room is at least 300 cubic feet per head ; but it is well to aim at a higher proportion. A room 12 feet long, 10 feet wide, and 10 feet high contains, when free from furniture and inhabitants, 1,200 cubic feet of air, and will therefore accommodate four healthy adults if adequate ventilation be provided.

Experiment 95.—Place a few pieces of ice in a test-tube ; the sides of the latter are soon cooled down nearly to the temperature of melting ice, and in turn they cool the air immediately in contact with the exterior of the tube ; moisture is then seen to be deposited on the glass, because air nearly saturated with aqueous vapour at a comparatively high temperature deposits much of its water when cooled nearly to the freezing point, or to any temperature below that at which the amount of vapour actually present would suffice to saturate it.¹ In nature, when this saturation point is passed, the excess separates in the form of dew, cloud, or rain. Therefore, by the attraction of deliquescent bodies and by the method of cooling, we learn that ordinary air contains aqueous vapour ; the amount of this is, however, extremely variable.

Experiment 96.—Fill a large glass beaker capable of holding two or three liters with fresh and clean rain water ; add to the water about 10 c.cs. of *Nessler test* solution,² and let the mixture stand after mixing. Few samples of rain water fail to show a pale yellow colour when treated with the test, which latter is the most delicate reagent for ammonia that we are acquainted with.³

¹ Air but three-fourths saturated with moisture is in the best condition for respiration. See Chapter XX. for estimation of moisture in air or other gas. A work on physics must be consulted for the general subject of *Hygrometry*.

² The preparation of this solution is described under Iodine. See page 100.

³ So delicate is this test that it will indicate the presence of 1 part of ammonia in 10,000,000 of water.

The ammonia (NH_3) in air rarely exceeds one part in one million; but this minute proportion, when carried to the soil by means of rain, amounts to between 5 and 6 lbs. per acre annually, and from this source vegetation on uncultivated soils derives some of the nitrogen necessary for healthy development, though, as the elaborate experiments of Messrs. Lawes and Gilbert at Rothamstead have shown, the agricultural importance of this aerial ammonia has probably been exaggerated.

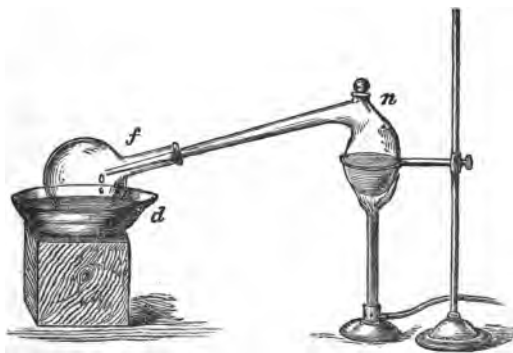
We have already (Experiment 69) learned how to test for ozone in air, and the characters of the other accidental constituents of the atmosphere already enumerated will best be dealt with under the several compounds.

CHAPTER XIV.

EXPERIMENTS WITH COMPOUNDS OF NITROGEN.

THE element nitrogen has been so named (see page 3) because it produces *nitre*, and is a characteristic constituent of that body. This nitre is a white crystalline compound which is found on analysis to contain

FIG. 60.



nitrogen, potassium, and oxygen, in the proportions indicated by the formula KNO_3 .

NITRIC ACID = HNO_3 .—*Molecular weight* = 63.

Experiment 97.—Place in a tubulated retort *n*, fig. 60, about 30 grams of nitre and well cover it with

strong sulphuric acid; connect the retort directly with the receiver *f*, which latter is supported by the dish *d* containing cold water; gently heat the retort and raise to the boiling point, a heavy fuming liquid of a yellow colour distils over and collects in the receiver, which latter should be occasionally cooled by pouring water over it. When the distillation is at an end allow the apparatus to cool, when the residue in the retort will solidify to a crystalline mass easily dissolved out by water, and consisting of acid potassium sulphate, KHSO_4 . The contents of the receiver are now to be examined.

a. Allow a drop of the liquid to fall on a piece of blue litmus paper; the latter is instantly coloured red and then bleached, while the paper is soon destroyed—therefore the liquid is a strong and corrosive *acid*.

b. If a piece of white silk, some wool, or cork be immersed in the acid it is quickly coloured yellow, and, in the case of the cork, soon destroyed. The skin is likewise corroded and stained yellow by the acid.

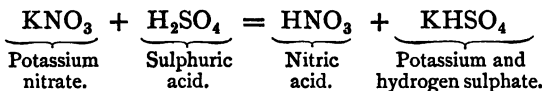
c. Add a few drops to a solution of *indigo*; the blue colour of the latter is instantly changed to a dirty brown.

d. Place a few fragments of copper in a test-tube and pour over the metal a small quantity of the acid. Deep ruddy fumes are rapidly evolved, and a blue liquid remains in the tube.

The acid possessing these characters is nitric acid, or *aqua fortis*, whose formula when pure is HNO_3 .

The following equation represents the change that

takes place when nitre and sulphuric acid are heated together—



On the large scale the cheaper sodium nitrate (NaNO_3) or 'Chili nitre' is used instead of the potassium compound ; moreover, in order to avoid waste of sulphuric acid, two molecules of the nitre for one of acid are used, but the heat required to complete the operation is much higher than that employed in the Experiment 97, and the residue in the large retorts used is neutral sodium sulphate, Na_2SO_4 —



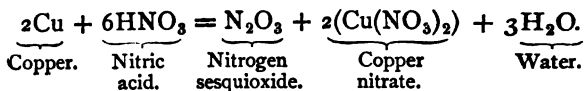
Pure nitric acid has a specific gravity of 1.510 (water = 1.000).¹

The best commercial acid is a colourless liquid of specific gravity 1.420, and contains about 30 per cent. of water. When exposed to the air it emits an acid corrosive vapour, and begins to boil when heated to 121° C.

The acid is distinguished by the characters and tests already observed, and we have in the copper test (d) an experiment illustrating the fact that nitric acid is a powerful oxidising agent, since it easily suffers deoxidation to a low oxide of nitrogen, to—

¹ The colour of the ordinary acid is due to the presence in solution of oxides of nitrogen ; these can be removed by making a stream of air bubble through the acid. Other impurities often found in the commercial acid are sulphuric and hydrochloric acids ; for their tests see the respective acids.

gether with loss of hydrogen. In the case of copper the reaction in the *strong* acid may be thus written—



The ruddy fumes observed in the experiments consist in part of the sesquioxide of nitrogen, and the blue liquid formed contains in solution the blue-coloured copper nitrate,¹ which latter can be separated by evaporation and crystallisation.

Experiment 98.—Put a lump of red-hot charcoal on any suitable support under a flue. Take up a few drops of strong nitric acid in a long glass tube and allow the acid to fall on the charcoal. Note that violent action at once takes place, the charcoal burning rapidly in the oxygen of the acid.

Experiment 99.—Add some of the acid to a solution of ferrous sulphate or ‘green vitriol;’ it at once communicates a *black* colour, which is changed to brown on boiling.² This is the *iron* test for nitric acid.

Experiment 100.—Place a crystal of the alkaloid *Brucia* on a white plate and let fall a drop of the strong acid upon it. Note that a fine *orange red* colour is developed.

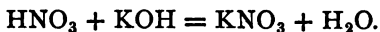
Experiment 101.—Place a few cubic centimeters of nitric acid in a capsule, and add caustic potash solution until the acid is neutralised ; then evaporate

¹ For the action of the weaker acid on copper, see page 35.

² For the explanation of this, see page 36.

Experiments on the Basicity of Nitric Acid. 27

until a pellicle forms and allow to stand. On cooling crystals of nitre separate—



The analyses of nitric acid and of nitre lead to the formulæ just given as the simplest expressions for their composition ; but the discussion of the analytical data cannot tell us whether nitric acid may not be represented by the symbols — $\text{H}_2\text{N}_2\text{O}_6$, and nitre by $\text{K}_2\text{N}_2\text{O}_6$, or some multiples of these values. Moreover, the vapour of nitric acid is so easily decomposed by a high temperature that Avogadro's law cannot help us to decide between the above formulæ. How then are we to proceed in order to determine which of the formulæ, HNO_3 or $\text{H}_2\text{N}_2\text{O}_6$, for example, is correct—in other words, whether nitric acid is *mono-* or *di-basic*? (See Part I. page 84.) A little consideration will satisfy us that if the acid be di-basic and its formula $\text{H}_2\text{N}_2\text{O}_6$, it ought to be possible to form a second potassium salt—one containing KHN_2O_6 . We must, therefore, make an experiment calculated to determine this point.

Experiment 102.—Take two porcelain capsules perfectly clean and dry, and place one on each pan of the balance and counterpoise exactly; then mark one capsule A and the other B, so as to know which pan it belongs to. Remove the capsules and place in each 10 c.cs. of the same strong solution of caustic potash coloured blue by the same quantity of solution of litmus. Now neutralise the potash in A by nitric acid added gradually, without loss, from any convenient measuring vessel. Note the quantity required for thi^o

purpose. Next add to the caustic potash in B *double* the quantity of the nitric acid required to just neutralise the first. Place the two capsules close together on a small tray of sheet iron, the bottom of which is covered with a layer of sand, and heat this 'sand bath' by means of a gas or spirit flame underneath, so as to make the liquid in each capsule slowly evaporate without boiling or spirting. When the solutions have been concentrated to the same extent small crystals separate ; no difference is observed in the appearance of these or in their apparent amount, but during evaporation acid fumes are freely evolved from B. Continue the gentle heat until a dry mass is left in each capsule and acid vapours are no longer given off ; then, when cold, replace the capsules in their respective balance-pans. If the operations have been carefully conducted the capsules should still counterpoise, proving that the *same weight* of matter was produced in each case ; and when each residue is carefully examined it is found to possess all the characters of nitre. If it were possible to form the salt KHN_2O_6 , it should have been produced in B and detected there by a great gain in weight and by differences in the characters of the salts obtained in the two capsules. No new salt is separated, but merely a mixture of nitre and excess of nitric acid is obtained, and the latter being volatile is driven off during evaporation. Therefore nitric acid is a mono-basic acid, and its formula must be written HNO_3 .

Experiment 103.—Introduce into a test-tube some copper turnings and nitre, add enough water to dissolve the latter, and heat. No fumes will be evolved.

Cool the liquid and add a cubic centimeter or so of oil of vitriol ; violent action soon begins and ruddy fumes are freely evolved, just as in Experiment 97, *d*. In this case the metallic nitrate is inactive ; but on addition of the powerful sulphuric acid the salt is decomposed as in Experiment 97, and the nitric acid thus set free at once produces its characteristic effects. For a similar reason a metallic nitrate reacts, as in Experiments 99 and 100, only after the addition of sulphuric acid ; hence this addition cannot be neglected in testing a salt of nitric acid.

Experiment 104.—Mix a very small quantity of nitre with about one-third of its weight of powdered charcoal in a small porcelain crucible, and apply heat. Violent action almost amounting to explosion takes place ; the mixture is said to ‘deflagrate’—the carbon or charcoal burning in the available oxygen of the nitre. All nitrates¹ cause this deflagration. When sulphur as well as charcoal is mixed with nitre, *gunpowder* is produced. The proportions of the ingredients differ somewhat, according to the purpose for which the powder is to be employed, but the percentage composition of good rifle powder is—

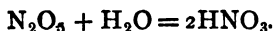
Nitre	75
Sulphur	10
Charcoal	15

Such a powder when fired affords about 280 times its volume of gas, corrected to 0° C. and 760 m.m. ; and this gas is found to be a somewhat variable mixture of nitrogen, carbon dioxide, and

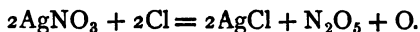
¹ For the characters of particular nitrates, see Part III.

carbon monoxide gases, with much smaller proportions of other gaseous bodies. A solid residue, rich in potassium sulphide, results from the decomposition, and this, when blown out into the air from the muzzle of a gun, quickly burns and forms potassium sulphate, of which the white smoke chiefly consists.

By the action of phosphoric anhydride on strong nitric acid, colourless crystals can be obtained containing N_2O_5 . This is nitrogen pentoxide, or nitric anhydride, and when added to water it reproduces nitric acid thus—



The same anhydride is produced when dry chlorine gas is conducted over dry silver nitrate; silver chloride and oxygen are likewise obtained—



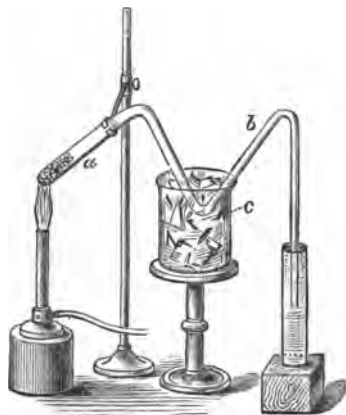
Poisonous action.—Strong nitric acid is a powerful corrosive, colouring the skin or mucous membrane yellow, and destroying the tissues. When swallowed it acts as a strong irritant poison and produces violent vomiting, great pain, loss of voice, difficulty of breathing, and ultimate death. When much diluted with water the acid can be safely taken in small quantity. *Antidotes.*—Calcined magnesia or dilute solution of borax, followed by oily or mucilaginous drinks.

NITROGEN PEROXIDE= NO_2 or N_2O_4 . *Mol. weight*=46.

Experiment 105.—Take a tube of hard glass closed at one end (*b*, fig. 61). Having introduced

about 10 grams of dry and powdered lead nitrate into *a*, bend the tube in the form shown ; then apply heat to the salt ; presently deep orange fumes are given off, and these pass down the tube *b*; if the bend *c* be immersed in a freezing mixture of ice and salt, or a mixture of hydrochloric acid and sodium sulphate,

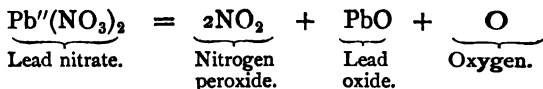
FIG. 61.



the fumes condense and form drops of a blue liquid, which solidifies to a white crystalline mass if cooled to -10° C. This body is an oxide of nitrogen whose formula in the state of gas is NO_2 ,¹ though often written N_2O_4 for reasons that will be stated when considering another oxide of nitrogen.

¹ When electric sparks are passed for some time through dry air, a mixture of oxides of nitrogen is formed, amongst which this body occurs.

The decomposition of the lead nitrate is thus represented—

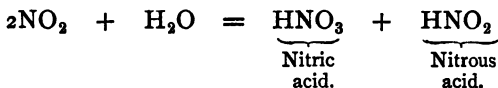


The oxygen gas is mixed with the nitrogen peroxide.

a. As the gas issues from the delivery tube make it bubble through *oil of vitriol*. Note that much of the ruddy fumes dissolve in the acid, the oxygen escaping.

b. Pass some bubbles through solution of *potassium sulphocyanate*; a transient red colour is produced.

c. Pass the gas into a small quantity of ice-cold water; it is absorbed and an *acid* liquid is obtained. NO_2 is not an acid anhydride, but it affords a mixture of acids which are directly related to two other oxides of nitrogen, thus—

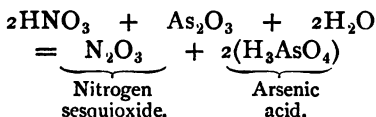


NITROGEN SESQUIOXIDE OR NITROUS ANHYDRIDE
 $= \text{N}_2\text{O}_3$. *Molecular weight*=76.

NITROUS ACID= HNO_2 . *Molecular weight*=47.

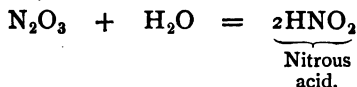
Experiment 106.—Introduce a gram or two of white arsenic (As_2O_3) into a tube similar to *a b*, fig. 61; add some nitric acid diluted with half its volume of water. On the application of a gentle heat brown fumes are given off; these, if cooled below 0°C ., afford a blue liquid, or when passed into ice-cold water, a blue

solution is obtained. The formula of the body is N_2O_3 . The reaction which affords it is thus expressed—



The arsenic acid remains in the tube. We have already seen (Experiment 97) that nitrogen sesquioxide forms a considerable portion of the gas evolved when *strong* nitric acid acts on copper.

a. Pass the oxide into water, and note that an *acid* solution is obtained, and this is found to contain but a single acid. In this respect N_2O_3 acts as an anhydride, like N_2O_5 , and affords a definite but very unstable monobasic acid, *nitrous acid*,¹ with the elements of water—



It will be remembered that this is one of the two acids already known to result from the action of NO_2 on water.

b. Add a few drops of the solution of nitrous acid to water coloured by a little Condy's fluid (solution of potassium permanganate, a body rich in oxygen with which it easily parts, and then loses its fine purple

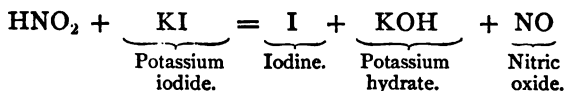
¹ The terminal *ous* as applied to an acid is always employed to indicate a less oxidised body than one whose name ends in *ic*. In the above case, nitrous contains less oxygen than nitric acid.

colour) ; the solution is decolorised and the nitrous converted into nitric acid, thus—



Therefore nitrous acid can act as a deoxidising or *reducing* agent. Now prove that nitric acid in dilute liquids does not decolorise the permanganate, by making a corresponding experiment.

c. Add a few drops of the nitrous acid to 200 or 300 c.cs. of water containing a little potassium iodide in solution and some starch paste—a *blue* colour will be produced if the solution be very dilute, or a greenish brown if strong. The colour is due to the element iodine which is set free by a portion of the nitrous acid, and then produces a strongly coloured 'iodide of starch.' In this case nitrous acid acts as an *oxidising* agent, thus—



and, while losing its hydrogen, parts also with an atom of oxygen, and is reduced to the lower oxide of nitrogen—nitric oxide. Another portion of the nitrous acid neutralises the potassium hydrate liberated in the above reaction.¹

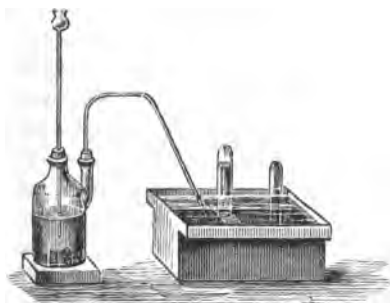
NITRIC OXIDE=NO or N₂O₂. *Mol. weight*=30 or 60.

Experiment 107.—Take the bottle, fig. 62, used

¹ Pure dilute nitric acid does not afford this reaction, and the two acids may therefore be distinguished by its means. In the application of this test to the detection of *nitrites* in well water the latter must be acidified with acetic acid.

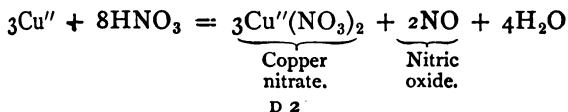
in the preparation of hydrogen gas, and introduce some copper turnings or wire into it, cover the metal with some warm water, and insert the cork carrying the thistle funnel. Now pour down the funnel tube a little strong nitric acid. Chemical action soon commences and much gas is evolved ; the first portions are allowed to escape, and the gas is then collected as usual in the jars. As the evolution of gas slackens, a

FIG. 62.



little more acid will make it brisk again. The jars of gas should be allowed to stand over the water for a short time in order that the brown fumes of N_2O_3 that generally accompany it may dissolve in the water and leave the gas colourless.

This gas is nitric oxide— NO , produced in the following reaction with the somewhat *diluted* acid—



a. Remove a jar full of the colourless gas, covered with its glass plate as usual. Withdraw the plate, and note that brownish fumes are instantly produced when the gas meets the air. This is the most characteristic property of the gas, as it rapidly passes into one or other of the higher oxides of nitrogen— N_2O_3 or NO_2 —on meeting with a sufficient proportion of *free* oxygen.

This property is of the utmost importance in the manufacture of oil of vitriol.

b. Place a piece of phosphorus in the spoon, fig. 63, and touch it with a warm wire; while it is just kindling or burning feebly, plunge it into a jar of nitric oxide—the flame is almost or quite extinguished. Now withdraw and again kindle, but let the phosphorus burn briskly, then plunge into another jar of the gas; vivid combustion now takes place. In the first case, the temperature was not sufficiently raised to decompose the gas and render its oxygen available; in the second this decomposition occurred, phosphoric anhydride was produced, and free nitrogen left. Similar experiments may be made with sulphur and wood.

FIG 63



c. Make a strong solution of ferrous sulphate (green vitriol) in water and pour the solution into a jar of the gas, close the mouth quickly with a glass plate or the hand, and shake. Note that absorption occurs, as the plate or hand is drawn tightly up to the mouth of the jar, and the contents of the latter become *dark-coloured*. Therefore the gas is easily soluble in solution of ferrous sulphate, though 100 c.cs.

of pure water dissolve only 5 c.cs. of the gas. A definite compound is formed in solution whose formula is NO_2FeSO_4 . If the dark liquid be boiled the nitric oxide is driven off as gas, and a somewhat brownish solution left. The above dark-coloured compound is formed in testing for nitric acid by ferrous sulphate (Experiment 99), the latter first deoxidises the nitric acid and the chief product of reduction—nitric oxide—then dissolves in the excess of sulphate.

Experiment 108.—Fill a tube of the form shown, fig. 64, with mercury, and invert in mercury in a stout tumbler; now introduce as much nitric oxide gas as will about half fill the tube. Pass up into the gas, through the mercury, a pellet as large as a pea of the metal potassium (the latter should be dried from adherent naphtha by blotting paper, and the surface then scraped clean with a knife). By closing the mouth of the tube under the mercury with the thumb, and giving a jerk, the potassium can be thrown into the end *a* without leaving any mercury there. Remove the thumb, keeping the tube still under the surface of the mercury and the end *a* depressed as shown, then apply heat to the potassium; the metal melts and quickly combines with the oxygen of the nitric oxide, leaving pure nitrogen gas. Allow the apparatus to cool and note that the mercury has risen in the tube. If the experiment be properly conducted the volume of gas is

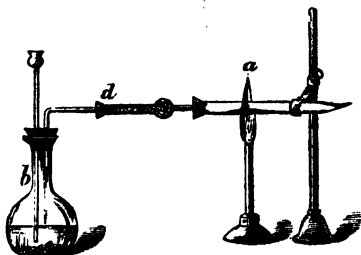
FIG. 64.



reduced *one-half* ; therefore nitric oxide contains only half its volume of nitrogen—that is to say, the molecule of nitric oxide contains but a semi-molecule (one atom) of nitrogen. We are not, however, justified in assuming that it contains only half its volume, or one atom, of oxygen ; hence another experiment is necessary.

Experiment 109.—Place some copper turnings in a glass tube similar to that used in Experiment 52. Heat the copper strongly, and pass over the metal a slow current of nitric oxide. Note that the copper is

FIG. 65.



blackened, while the issuing gas does not become brown when mixed with air, but exhibits the properties of nitrogen when collected and examined. The oxygen is abstracted by the copper just as in the former experiment with potassium. If the copper be weighed before and after experiment, the gain in weight represents the oxygen derived from the nitric oxide ; and if the volume of the latter be known, we have but to find the *volume* that corresponds to the weight of oxygen abstracted ; this proves to be but *half* that of

the nitric oxide, hence the latter contains half its volume of nitrogen and half of oxygen.

The molecule of nitric oxide is therefore made up of one atom each of nitrogen and oxygen, and its specific gravity, 14.99, confirms this conclusion, for $14.99 \times 2 = 29.98$ is the molecular weight of the gas, or the weight of two *vols* in centigrams; now one *vol* we know to be nitrogen weighing 14 centigrams, and one *vol* oxygen weighing 16 centigrams, and $16 + 14 = 30$. Therefore the formula of the gas is certainly NO.

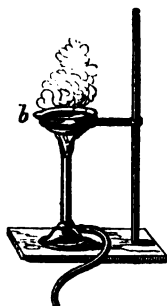
But the nitrogen atom is pentad, or five-link, and that of oxygen diad, or two-link, and no possible combination of these single atoms can give us anything but an unsaturated molecule with one link unattached; thus we have a remarkable exception to the general rule that free molecules have all their links (i.e., centres of attraction) of their component atoms engaged. Some chemists, in order to get over this difficulty, write the formula N_2O_2 , assuming that the two *quasi* monad NO groups satisfy one another; but this is, as we have seen, contrary to the molecular weight according to Avogadro's law. Curiously enough, nitrogen peroxide gas is also an exception, for its composition and specific gravity at temperatures far above its condensing point lead to the formula NO_2 , which is irregular like NO, but when the gas is cooled down its specific gravity increases from 23 ($H = 1$) to nearly 46 when close to the condensing point—the latter number gives the molecular weight 92 and the formula N_2O_4 . Thus the combination assumed in the case of nitric oxide can be distinctly

traced in that of nitrogen peroxide ; nevertheless, the simpler formula for each gas is that which best represents the composition at ordinary temperature and pressure.

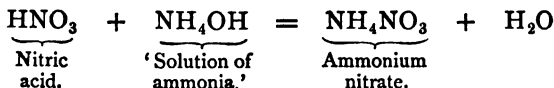
It must be remembered, however, that the existence of exceptions such as those pointed out do not invalidate the general rule stated, but they serve to show that the law according to which 'links,' 'bonds,' or 'atomicities,' as they are variously called, disappear, is yet but imperfectly known.

NITROGEN MONOXIDE (*Nitrous oxide, or laughing gas*) = N_2O . 1 Vol weighs 21.99 c.grs. Molecular weight = 44.

FIG. 66.



Experiment 110. — Pour some 30 or 40 c.cs. of strong nitric acid into an evaporating basin (see fig. 66) ; dilute with an equal volume of water, and add gradually the strong commercial 'solution of ammonia' until the acid is neutralised ; this point is ascertained by test-paper in the way already described. The liquid in the dish is now a solution of ammonium nitrate—

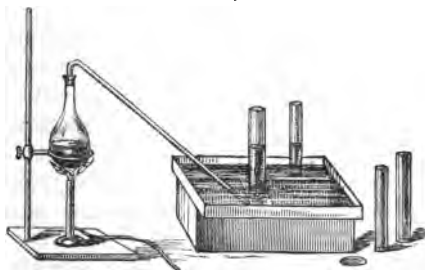


The nitrate is obtained in the solid state by evaporating the solution to dryness ; the residue

when cold, is removed from the basin and preserved in a well-closed bottle, as it is a deliquescent body.

Experiment 111.—Fit up a Florence flask as for the preparation of oxygen (fig. 67). Introduce into the flask about 30 grams of the ammonium nitrate, prepared as just described, and having inserted the cork carrying the delivery tube, and filled the pneumatic trough with *hot* water (*vide c*), apply heat. The salt melts, and evolves much gas and steam as the temperature reaches 230° C. The gas is termed

FIG. 67.



nitrous oxide ; when its evolution commences the heat must be carefully applied, so as to avoid a too rapid and dangerous decomposition. Collect several jars of the gas, and at once remove the delivery tube from the water. The gas in the jars is generally cloudy at first, owing to particles of saline matter carried over in the current, but it soon becomes clear ; note that it is colourless.

a. Remove a jar, and plunge into the gas a burning taper ; its combustion is much more rapid than in air.

b. Into another jar of gas plunge burning phos-

phorus, carbon, wood, or sulphur, and note that nearly as vivid combustion ensues as in oxygen; but all the bodies, more especially sulphur, require to be burning strongly in air before they are brought into the gas, else they are extinguished.

c. Transfer a jar of gas to a vessel of cold water; allow about one-fourth of the gas to escape, then firmly close the mouth of the jar while under water with the hand, and shake up the gas with the water enclosed in the jar. The hand will be drawn against the mouth of the jar, and on bringing the latter under water and removing the hand the proportion of gas to water will be considerably reduced, indicating that some of the gas has dissolved. By repeating this treatment several times, the gas, if free from air, will be completely absorbed. Therefore this gas, unlike oxygen, is tolerably soluble in cold water; in fact, 1.00 c.c. of water at 15° C. dissolves 0.7778 c.c. of the gas,¹ but it does not dissolve in water near to the boiling point.

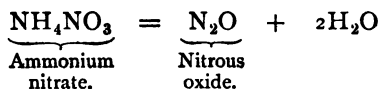
Experiment 112.—Heat some potassium in a tube of this gas, exactly as described for nitric oxide in Experiment 108, and note that the gas does not diminish in volume after evident decomposition by the metal, and the residual gas possesses the properties of pure nitrogen. Therefore the molecule of this gas, unlike that of nitric oxide, contains *its own volume of nitrogen*.

By the method adopted in Experiment 109 it can be shown that this gas, like nitric oxide, contains half

¹ 1.00 c.c. of alcohol at the same temperature absorbs 3.267 c.cs. of the gas.

its volume of oxygen. It therefore contains, for the same volume of oxygen, twice as much nitrogen as nitric oxide, and its formula is N_2O .

The change that takes place on heating ammonium nitrate is therefore represented by the equation—



The molecular weight of the body should be $44 = (14 \times 2) + 16$, and its specific gravity ($H = 1$) ought to be $\frac{44}{2} = 22$. The experimental number is 21.99 ; therefore the above formula is correct. Consequently 1 vol weighs 21.99 c.grs. at 0°C. and 760 m.ms.

Experiment 113.—Take a jar, that we may call A, containing only air, and hold it mouth upward. Take a jar, B, of N_2O , and turn it mouth upward also and remove its plate. Now slowly pour the gas from B into A, just as you would pour a liquid from the vessel, and test both jars with a taper having a glowing wick. The taper is re-kindled in A, but not in B, thus proving that the gas is so much heavier than air (1.52 times) that it can displace the lighter air just like liquid. The gas cannot be retained in an open vessel for any length of time, as it escapes by diffusion (see Experiment 92) into the atmosphere. It is liquefied by a pressure of 30 atmospheres at 0°C.

The gas is often termed *laughing gas*, in allusion to the curious property Sir Humphry Davy found it to possess, when mixed with some air and inhaled, of causing temporary excitement and a sense of

exhilaration. When unmixed with air or oxygen, and pure,¹ nitrous oxide produces insensibility if inhaled for a short time; at first ringing noises are heard and a 'general sense of pulsation' is experienced, then sleep supervenes, during which any short operation, such as the extraction of a tooth, can be and frequently is performed. A few full respirations of pure air restore the patient, and no unpleasant after-effects follow the administration. In the latter respect nitrous oxide is superior to ether and chloroform as an anæsthetic (i.e., a body used to procure insensibility to pain), but the gas can completely suffocate if too long inhaled. Ringer says of it: 'It appears to me to produce its anæsthetic effect by preventing oxidation of the nervous centres, and this chiefly by depriving the blood of its supply of free oxygen from the air.' Although there is *more* oxygen in nitrous oxide than in air,² it is chemically combined with nitrogen, and thus we have, in the comparative action of nitrous oxide gas and air on the animal economy, a remarkable illustration of the wide difference in characters that may exist between a chemical compound and a mechanical mixture of the same elements.

We have thus recognised the existence of five oxides of nitrogen, two of which are anhydrides of distinct acids. If we assume that the molecule of

¹ Nitrous oxide gas intended for inhalation should be purified from ammonia and higher oxides of nitrogen by obliging it to pass in succession through sulphuric acid and solution of ferrous sulphate, or green vitriol, contained in suitable wash-bottles.

² 38.6 per cent. by weight, as against 23 per cent. in air.

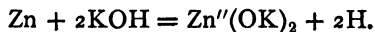
each oxide contains the same weight (i.e., 28 parts) of nitrogen—although we know this is not quite true in one instance at least—it follows that the group of known oxides of nitrogen is a complete series of compounds resulting from successive additions of single oxygen atoms to the lowest term—i.e., nitrous oxide. Thus—

Nitrous oxide	.	.	.	N_2O
Nitric oxide	.	.	.	N_2O_2 , or NO .
Nitrogen sesquioxide, or nitrous anhydride	.	.	.	N_2O_3
Nitrogen dioxide	.	.	.	N_2O_4 , or NO_2
Nitric anhydride	.	.	.	N_2O_5 .

In this group of bodies we therefore have additional evidence in support of the law of *multiple proportions* already deduced from the examination of the two oxides of hydrogen. (*Vide* Part I. under Experiment 80.)

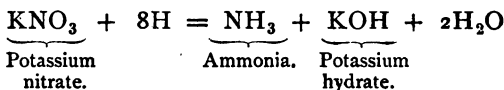
AMMONIA = NH_3 . 1 Vol weighs 8.5 c.grs.
Molecular weight = 17.

Experiment 114.—Boil some metallic zinc with strong caustic potash solution in a large test-tube; the metal slowly dissolves and a gas is evolved which burns at the mouth of the tube, and can be easily shown to be hydrogen, and *zinc potassate* is left—



On the addition of a few drops of nitric acid or a little *nitre* to the solution and again heating, the pungent smell of *hartshorn* is noticed, and a piece of

red litmus-paper held in the current of steam is rendered blue, proving the presence of an *alkaline* vapour. We may anticipate the results of some future experiments by stating that in this case a portion of the hydrogen, no longer set free, but when in the *nascent*¹ state, quickly deoxidises the nitre, forming therewith water, while another portion unites with the nitrogen of the nitre and forms *ammonia* gas, which latter is evolved, while potassium hydrate is left in solution. Thus—



Experiment 115.—Pass a current of gaseous hydrogen through a hot alkaline solution of nitre, and test the issuing gas with reddened litmus-paper. No trace of alkaline ammonia can be detected if the materials employed are pure, and care be taken to prevent any of the liquid reaching the paper.

These two experiments well illustrate the difference in activity between the comparatively stable free molecule of hydrogen and the same element in the *nascent* condition—i.e., at the moment of liberation of its atom from a compound, and, as some suggest, before it can meet with another atom in order to form the gaseous molecule. Many other cases of a similar kind will be met with later on.

Experiment 116.—Take a tube of hard glass closed at one end, and one-third fill it with pieces of horn, bone, gelatine, feathers, wool, hair, or, if the

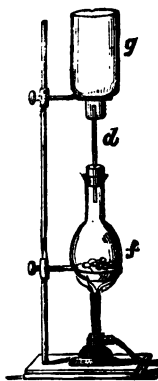
¹ From *nascor*, to be born.

tube be a large one, fragments of coal, and apply heat. The organic or carbonised matter soon decomposes under the influence of the heat, and various volatile and strongly smelling products are obtained, amongst which *ammonia* may be recognised by its power of changing the colour of red litmus-paper to blue. All the bodies mentioned agree in containing nitrogen—even coal contains from 1 to 2 per cent.—and, during the above process of *destructive distillation*¹ by heat, it combines with hydrogen, likewise present, and forms ammonia. All nitrogenised animal and vegetable bodies afford more or less ammonia in this way, not only at high but at ordinary temperatures, when they undergo slow putrefactive change or decomposition in presence of moisture—in fact, much of the atmospheric ammonia is derived from these sources.

Most of the ammonia employed in the arts is obtained from the tarry ammoniacal liquors collected during the manufacture of coal gas. The preparation of *sal-ammoniac* and similar compounds from these solutions will be referred to under 'Salts of Ammonia' in Part III.

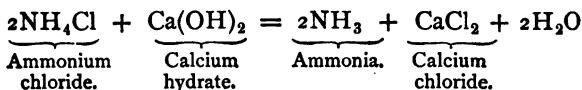
Experiment 117.—Coarsely powder some *sal-ammoniac*, or ammonium chloride (NH_4Cl), and mix it with rather more than its own weight of slaked

FIG. 68.



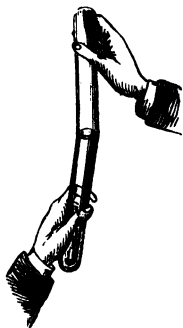
¹ Or distillation attended by decomposition.

lime in fine powder, quickly transfer the mixture to the flask *f*, fig. 68, insert the cork carrying the delivery tube *d*, and invert over the free end of the latter the dry bottle *g*. On applying a very gentle heat to the mixture in *f*, abundance of ammonia gas is evolved, the pungent smell of which is quickly perceived, while red litmus-paper passed up into the gas is instantly turned blue, and white fumes are produced when a glass rod, moistened with hydrochloric or acetic acid, is brought to the mouth.¹ Note that the pure gas is colourless.



- a.* Pass up a lighted taper into a jar full of ammonia. The flame is extinguished without igniting the gas.

FIG. 69.



- b.* Take a dry gas jar and attach a piece of red litmus-paper near the top inside by means of gum. Invert the tube, and bring under its mouth a rather larger tube full of ammonia gas, as shown in fig. 69, and slowly invert the latter. The colour of the litmus in the upper jar quickly changes, proving the ascent of the ammonia, and the flame of a taper is ex-

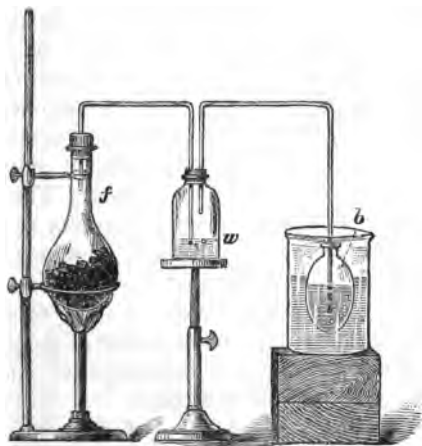
tinguished if passed up into the gas. Therefore am-

¹ Any other ammoniacal salt may be used instead of the chloride, and potassium or sodium hydrate instead of lime.

monia is lighter than air, and displaces the latter from the upper jar. Its specific gravity is 8.5 ($H = 1$), or but little more than half (0.586 if air = 1) as heavy as air.

c. Fill another stout bottle with the gas, close with a glass plate, and remove, still mouth downwards, to some water; withdraw the plate when the mouth

FIG. 70.



is under water. Note that the water rapidly rushes into the jar and nearly fills it; therefore ammonia gas is very soluble in water—in fact, 1 c.c. of water at 15°C . and 760 m.ms. dissolves 783 c.cs. of ammonia gas, or 783 times its volume.

Experiment 118.—Prepare ammonia gas as before, but wash it from impurity by making it pass

through the small quantity of water¹ in the little wash-bottle *w*, fig. 70, and then conduct the gas into a measured quantity of water contained in the bottle *b*, which latter is cooled by immersion in a beaker of cold water, as heat is evolved during absorption of the gas. Apply heat to the flask *f*, and pass the gas through the water in *b* as long as it is absorbed, but when bubbles pass through without sensibly diminishing in size it may be concluded that all the gas has been dissolved that the water can hold at the particular temperature and pressure. Measure the bulk of the liquid in *b* after the experiment, and it will be found to have increased to the extent of about one-half its volume.² This 'solution of ammonia' is colourless, with a characteristic and very pungent smell, and strong *alkaline* reaction to test-papers. The specific gravity of the solution is about 0.88 (water = 1).

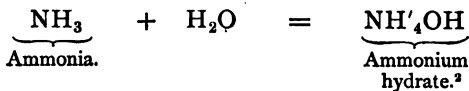
When the solution is heated, ammonia gas is expelled, and after boiling for a short time almost every trace of the gas is removed; thus 'solution of ammonia' is a very convenient source of the gas, and we shall use it presently for this purpose. Ammonia gas is also easily soluble in alcohol.

The extraordinary solubility of ammonia gas in water, accompanied as it is by considerable evolution of heat, is commonly regarded as due to true chemical combination—a new body being formed which closely

¹ Rather more than 50 c.cs. of water should be used for every 100 grams of sal-ammoniac.

² The process employed on the large scale in the manufacture of '*liquor ammonia fortior*' of the British Pharmacopoeia is identical with that given above.

resembles potassium and sodium hydrates in its highly alkaline character and power of neutralising acids (e.g. nitric acid, Experiment 110), and forming salts analogous to those of potassium and sodium; hence the liquid may be fairly regarded as a hydrate similar to those of the metals above named, in which hydroxyl is united to a monad compound radicle NH'_4 , which acts like a monad metal and is termed *ammonium*.¹ Thus—



Water saturated with ammonia gas at 0°C. , and under the pressure of 760 m.ms., may be regarded as nearly pure ammonium hydrate, since it contains a weight of ammonia equivalent to about 96 per cent. of NH_4OH . But a slight elevation of temperature suffices to decompose this body, and nearly all the gas can be expelled before the liquid reaches 100°C. Thus—



From the above experiments we learn how to prepare and to recognise ammonia gas, and to obtain 'solution of ammonia' of the British Pharmacopœia, or ammonium hydrate.

Ammonia can be condensed to a colourless liquid by cooling the gas to a temperature of -40°C. or F.

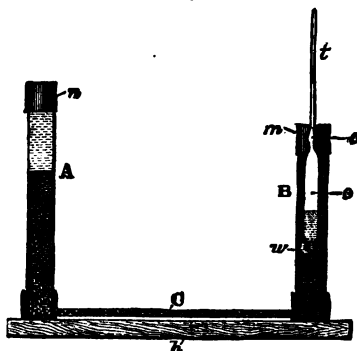
¹ See further, Experiment 124.

² Another compound is known, which is intermediate in composition between NH_3 and NH_4OH ; its composition is represented by the formula NH_2OH , and it is called *hydroxylamine*, since in it one atom of the hydrogen of ammonia has been replaced by the group OH or hydroxyl.

(and, it may be stated, this particular temperature is the only one indicated by exactly the same value on the Centigrade and Fahrenheit thermometer scales) by means of a freezing mixture of two parts of snow and three parts of crystallised calcium chloride.

The comparative ease with which ammonia gas can be liquefied by cold leads to the presumption that it admits of liquefaction by very moderate compression at ordinary temperatures. By means of the following

FIG. 71.



cheap and effective apparatus we can reduce the gas to the liquid form.

Experiment 119.—A species of U tube of stout wrought iron is made of the form shown in fig. 71, *A C B*. *A* is about 40 centimeters long, *B* 30 centimeters, and each is 2 centimeters internal diameter; *C* is about 25 centimeters and 5 or 6 millimeters internal diameter, and is securely screwed into the two wider tubes. The whole is fastened to the wooden stand *h*. *A* is provided with a stout screw-cap *n*, the joint

being rendered gas-tight by a leather washer. *B* is also fitted with a strong screw-cap with a deep head, through which a conical hole is bored ; the long glass tube *t* of the apparatus *t o* passes through this hole to the expansion *c*, which should fit into the cone and be there secured by any good cement. The screw-cap *m* therefore carries the glass apparatus, which latter is a form of pressure tube now easily obtained through good instrument-makers. The liquefaction is to take place within the glass tube *t*, which must of course be very strong ; the length of this tube is about 25 centimeters, and at first it is open ; the wide reservoir *o* must have at least ten times the capacity of *t* ; the reservoir *o* terminates below in a rather narrow curved tube *w*, which is always open. The glass apparatus must be filled with dry ammonia gas by connecting *w* by means of a flexible tube with *f*, fig. 70, affording a current of ammonia gas, but freed from moisture by passing through a long tube packed with fragments of fresh quicklime. When all air has been expelled—and a good current maintained for ten minutes is sufficient to effect this—the flow of gas is allowed to slacken and the capillary end of *t* securely sealed at the blowpipe ; the tube is removed from *w* and the latter at once dipped in mercury, which enters and prevents escape of ammonia.

Now remove the cap *n*, and pour mercury into *A* until the metal rises nearly to the top of *B* ; then introduce *o* into *B*, allowing the mercury displaced to overflow into a vessel placed to receive it, and screw home the cap *m* (which of course must be provided with a good leather washer). We have, therefore.

nothing but mercury between the gas in *o* and the surface of the metal in *A*. Next remove enough mercury from *A* by a pipette to leave a space of some 12 centimeters between the surface of the metal and the cap; then fill up to the top with the strongest 'solution of ammonia,' and screw down the cap *n*, and the apparatus is ready for experiment, which is performed in the following way:—

Gradually heat the portion of *A* containing the solution of ammonia by a Bunsen flame occasionally applied; as the temperature rises, ammonia is expelled from the solution, but since the gas has no escape, considerable pressure is exerted in *A* on the surface of the mercury, and the latter, acting as a fluid piston, compresses the gas in *o*, which steadily diminishes in volume until at last the mercury rises into view in *t*;¹ and if the heating of *A* be now carefully managed, the compression proceeds until a layer of colourless liquid is seen to form on the surface of the mercury in *t*. This is the liquefied ammonia, and is obtained when the pressure reaches about 6.5 atmospheres at mean temperature.

If the joints are well made and the heating well managed, it is easy to maintain a steady pressure for a considerable time, but anything like violent heating must at all times be carefully avoided. On allowing the apparatus to cool, the mercury recedes in *t*, and the liquefied ammonia disappears. This apparatus is always ready for experiment, though it is desirable to

¹ It is well to cover *t* with a large cage of fine wire gauze, lest the glass should give way when first subjected to considerable pressure.

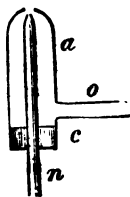
unscrew the cap of *A* occasionally and change the solution of ammonia, as slow leakage from *n* is inevitable.¹

Experiment 120.—As we have already seen (Experiment 117, *a*) ammonia does not burn when a light is applied to the cold gas. Now pass it through a narrow glass tube heated to redness near to the point at which gas issues, and it can be easily ignited, burning with a greenish-yellow flame in the oxygen of the air; it produces nitrogen gas and *water*, hence a cold body introduced into the flame is quickly bedewed with moisture—



Experiment 121.—A similar result is obtained if a stream of cold ammonia gas (obtained by heating some 'solution of ammonia') issuing from a jet be surrounded by oxygen gas and then ignited. The little apparatus, fig. 72, enables this experiment to be easily performed. *a* is a short brass tube into which oxygen gas can be admitted through the side tube *o*; *n* is a glass tube delivering ammonia; this passes through the cork *c*, which fits the brass tube *a*. Ammonia is allowed to flow through *n*, and then oxygen gas, derived from a bag or gas-holder, is turned on cautiously,

FIG. 72.



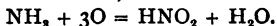
¹ As the use of a pressure pump is altogether avoided in this apparatus, it is inexpensive. Before using any form of apparatus for experiments of the kind described, it should be fully tested by the maker, and then should only be used by a careful manipulator.

while a flame is applied to the jet. When the proportions of the two gases are properly adjusted a tolerably steady flame can be obtained.¹

If in the last two experiments, but more especially in Experiment 120, we dry the ammonia by passing the gas through a tube filled with fragments of *quick-lime* (CaO), the appearance of water as a product of combustion is proof that hydrogen is a constituent of ammonia, while the mode of generating the latter from nitre adopted in Experiment 114 leaves little doubt that nitrogen is another constituent of the body; but the following experiment affords us complete evidence of the composition of ammonia.

Experiment 122.—Fill the eudiometer (fig. 73) one-fourth with say 20 c.cs. of dry ammonia gas over mercury. Measure the volume and pass a series of sparks from an induction coil between the wires within the tube.² The confined gas is thus intensely heated

¹ In these experiments the rapid oxidation of ammonia involves complete decomposition; but when slowly oxidised, especially in aqueous solution, it first affords nitrous acid, thus—



The nitrous acid then unites with another atom of oxygen, and produces nitric acid, thus—

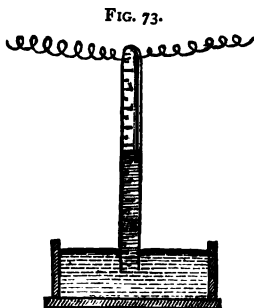


The organic matter of sewage readily affords ammonia on decomposition, and the latter then undergoes slow oxidation as just stated; hence in sewage-contaminated water *nitrites* and *nitrates* are usually to be found.

² In this case a Leyden jar must be placed in circuit in order that the maximum heating effect may be obtained. For this purpose it is merely necessary that one of the coil wires should be in metallic connection with the knob, and the other with the external coating of the jar.

and decomposed, and if the sparks are passed for a sufficient time the volume of gas increases to 40 c.cs., or is *doubled*. Having obtained the maximum expansion, note the volume, and introduce 20 c.cs. of pure oxygen and explode in the usual way. After correcting for alteration of level, the residual gas will measure only 15 c.cs.; therefore $60 - 15 = 45$ c.cs. of gas have disappeared, two-thirds of which, or 30 c.cs., must be hydrogen and the rest oxygen (see Experiment 24).

As 20 c.cs. of oxygen were introduced, and 15 c.cs. have thus disappeared in union with hydrogen, the residual gas in the tube must contain 5 c.cs. of oxygen. This residue measures, as we have seen, 15 c.cs.; hence $15 - 5 = 10$ c.cs. of nitrogen left.¹ To sum up, then, our experiment proves, firstly, that ammonia gas contains only nitrogen and hydrogen; secondly, that it is completely decomposed into its constituents at a high temperature; thirdly, that the resulting mixture of gases occupies twice the volume of the original ammonia; fourthly, that this gaseous mixture contains one volume of nitrogen and three of hydrogen—consequently the molecule of am-



¹ By passing up a few drops of caustic potash, followed by a strong solution of pyrogalllic acid (see Experiment 83), the oxygen is absorbed and nitrogen only is left in such a condition that it can be easily identified.

monia gas contains one atom of nitrogen and three atoms of hydrogen, and must be represented by the formula NH_3 ,¹ and its molecular weight by 17

FIG. 74.

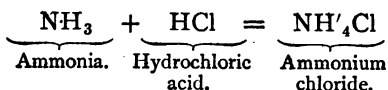


(14 + 3). This result is confirmed by the specific gravity of the gas, which, as we have already seen (page 49), is 8.5, and $8.5 \times 2 = 17$. 1 vol of ammonia gas (112 c.cs. at 0° C. and 760 m.ms.) weighs 8.5 c.grms.

Experiment 123.—Pour a few drops of strong commercial hydrochloric or ‘muriatic acid’ into a wide-mouthed bottle; cover with a glass plate and turn the bottle about so as to distribute the acid over the sides. Fill another bottle with ammonia gas, bring its mouth down on the glass plate that covers the first, as shown in fig. 74, and then remove the plate from between them so as to leave them mouth to mouth. White fumes are instantly formed in abundance, and they deposit a white saline body on the glass after a time which is

¹ We can recognise the nitrogen acting as a one-link, or monad atom, in nitrous oxide, $\text{N}'-\text{O}''-\text{N}'$, or N_2O ; as a three-link, or triad, in ammonia, $\text{N}'''\text{H}'_3$, and as a five-link, or pentad, in ammonium hydrate, $\text{N}'''\text{H}'_4(\text{OH})'$, the monad group hydroxyl, OH' , satisfying the fifth link. In the case of sal-ammoniac, $\text{N}'''\text{H}'_4\text{Cl}'$, we also have evidence of the five-link or pentad character of the nitrogen atom. In all these cases the links or bonds appear or disappear in pairs.

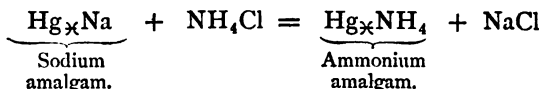
identical with sal-ammoniac or ammonium chloride, for



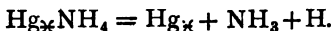
Thus at the commencement of our experiments we decomposed or *analysed* sal-ammoniac, and now we have reformed it or effected its *synthesis*, and we have written the formula of the body in such a way as to indicate that it is the chloride of the compound radicle ammonium NH'_4 , already referred to under Experiment 118, rather than NH_3HCl , the formula directly justified by its mode of formation. Now the former view assigns to the group NH'_4 a pseudo-metallic character, and it may be fairly asked whether ammonium has been isolated, and, if so, whether it presents any of the metallic characters. As a matter of fact, ammonium, NH'_4 , is not known in the *free* state, but a curious body can be prepared which is supposed to be a solution of ammonium in mercury. This body is easily obtained in the following way.

Experiment 124.—Introduce about one cubic centimeter of mercury into a wide test-tube; gently warm the metal over a lamp and, directing the mouth of the tube away from the person, drop in a fragment of clean metallic *sodium* about half the size of a pea. If the mercury be warm enough, the sodium will at once dissolve in it with a little explosion—if not, heat gently. Then introduce another piece of sodium of the same size, and after its solution a third. A silvery white *amalgam* of sodium is thus prepared.

which retains the metallic lustre.¹ Now pour out the warm and still liquid amalgam (for if allowed to become cold it will become pasty or solidify) into about 250 c.cs. of a cold saturated solution of sal-ammoniac (see Experiment 73). The amalgam quickly increases to at least 15 times its original bulk, and ultimately becomes a large pasty mass, light enough to *float* on the surface of the liquid. This mass can be removed and washed with water; it presents a brilliant metallic appearance, but it is very unstable and soon decomposes, evolving ammonia and hydrogen gases, and after some time nothing remains but the original mercury. This body appears to be a true amalgam of mercury and the metal-like ammonium, the latter taking the place of the sodium; thus—



The amalgam then breaks up in the following way—



There is therefore some experimental evidence as to the existence of the compound metal ammonium, and the close analogies traceable between its saline and other compounds and those of potassium and sodium confirm this view; but it would lead us too far out of our course to examine this question here;

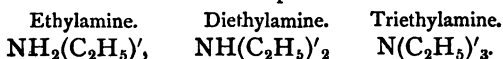
¹ Alloys of metals with mercury are termed *amalgams*; in some cases these are mere mixtures of metals, in others feeble chemical union takes place, but the product in all cases retains the metallic appearance.

hence we shall reserve this part of our study until we have to deal with the compounds of the alkali metals in Part III.

Experiment 125.—Powder half a gram or so of iodine and add it with frequent stirring to 20 c.cs. of ammonium hydrate solution ; allow it to stand for half an hour until a black powder has completely subsided, then pour away the clear liquid and distribute the black residue on pieces of bibulous paper. Put these in some safe airy place to dry. When the black substance is dry, a touch suffices to make it *explode*, when violet vapours of iodine are evolved. If small quantities are operated upon and reasonable care exercised, the experiment is not attended with danger.

The black substance is called *iodide of nitrogen*, and is really a mixture of ammonia derivatives. Dr. Gladstone's formula for the chief substance is NHI_2 , or ammonia in which two-thirds of the hydrogen has been replaced by iodine. Analogous bodies are produced by the action of chlorine (chloride of nitrogen) and of bromine (bromide of nitrogen) ; but these are amongst the most dangerous explosives known, and have caused so many serious accidents that any description of their preparation is undesirable.

Many other derivatives of ammonia are known in which various groups of elements replace one or more atoms of hydrogen in NH_3 ; these will be met with later on in our course, but we may here give the formulæ of three of these important bodies—



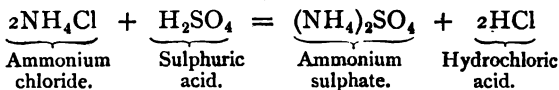
CHAPTER XV.

EXPERIMENTS WITH HYDROCHLORIC ACID AND
CHLORINE.

HYDROCHLORIC ACID (*Muriatic acid*) = HCl. 1 Vol of gas weighs 18.19 c.grs. Molecular weight = 36.5.

Experiment 126.—Mix some sal-ammoniac—ammonium chloride, as we shall term it for the future—with strong sulphuric acid in a test-tube. Even without heat a quantity of gas is evolved which has a very pungent smell and fumes in the air; it does not burn or support combustion of a match, but it *reddens* blue litmus-paper, and produces white clouds if a rod moistened with ammonium hydrate be brought near the mouth of the tube.

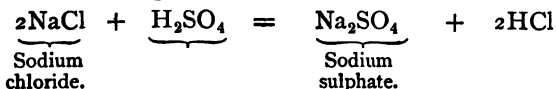
The gas evolved is therefore an *acid* gas capable of uniting with the alkaline ammonia, and this body is termed *hydrochloric acid*, and its symbol is HCl. Thus, in Experiment 117, we liberated ammonia gas from NH_4Cl , and in Experiment 123 re-formed the latter by effecting the combination of ammonia with hydrochloric acid. We have now broken up the compound again, but in such a way as to make it yield its acid constituent; thus—



In this case, each group, NH_4 , takes the place in

the sulphuric acid of one atom of H, and the latter unites with the Cl of the ammonium salt and forms the acid. The specific gravity of hydrochloric acid gas, determined as in Experiment 27, is 18.19 ($H=1$); and 1 vol weighs 18.19 c.grms. Its molecular weight is therefore 36.5 (if $Cl=35.5$).

Experiment 127.—Make a similar experiment with common salt or sodium chloride, and note that the same acid gas is evolved. In this case

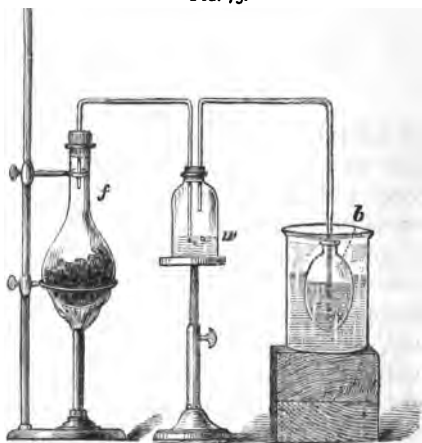


Lower the test tube from which HCl gas *freely* issues into a small dry gas jar standing mouth upwards, and loosely cover with a glass plate. After a minute or two slip aside the glass plate, rapidly remove the test-tube, and pour in a few cubic centimeters of water; cover the mouth with the hand and shake up. Note that a vacuum is produced, as evidenced by suction of the hand, indicating that the gas has been absorbed by the water; now test the latter with blue litmus-paper and note that it has acquired an acid reaction. Therefore hydrochloric acid gas is soluble in water and produces an acid liquid. As a matter of fact, the gas is very soluble in cold water, as we shall find presently, for 1 c.c. of water at 15° dissolves 450 c.cs. of the gas at the same temperature. It is a strong solution of the gas in water that constitutes the liquid hydrochloric acid ('muriatic acid' or 'spirit of salt') of commerce.

Experiment 128.—A glass flask, *f*, fig. 75, is provided with a cork through which passes the gas

delivery tube bent twice at a right angle and passed to the bottom of the wash-bottle *w*, which contains a very little water, which a tube leads from *w* into a bottle *b* containing cold distilled water. Place about 50 grams of common salt or sodium chloride in *f* and 50 c.cs. of water in *b*, and connect the apparatus as shown. Measure 50 c.cs. of oil of vitriol and add it gradually

FIG. 75.



and with stirring to an equal volume of water contained in a porcelain dish ; when cool, pour into the flask, and then, if necessary, apply a gentle heat to *f*. HCl is freely evolved as a *colourless* gas and passes through the water in *w*, where the first portions are absorbed, and then into the water in *b*. When all air has been expelled from the solution, the bubbles that pass into the water disappear before they reach the surface, the

gas is so easily soluble in water ; but when the latter is saturated they pass through without apparent diminution of bulk, and thus the end of the process can be recognised. The bottle *b* must be kept cool throughout, resting in the beaker of cold water.¹

When the gas is being freely evolved it is well to remove the delivery tube from *b*, dry it, and pass it to the bottom of a gas jar placed mouth upwards and partially covered with a glass plate. When the jar is judged to be full of the gas, remove the tube, close the mouth and bring it under water. The latter quickly rushes up and almost fills the jar, or quite fills it if all air has been expelled.

The solution ultimately obtained in the bottle *b* is a nearly colourless and strongly acid liquid, emitting white fumes which have a pungent smell. Its specific gravity is about 1.16 (water = 1.0), and it contains about 32 per cent. by weight of actual HCl. When heated this acid loses gas until the percentage of HCl is reduced to 20.24, and a solution of this strength boils at a constant temperature of 110° C. if the pressure does not vary from the normal (760 m.m.).

The common 'muriatic acid' of the shops always has a yellow colour, owing to the presence of *iron* ; other impurities commonly present are free chlorine, arsenic and sulphur compounds. Appropriate tests for these impurities will be found under their respective heads.

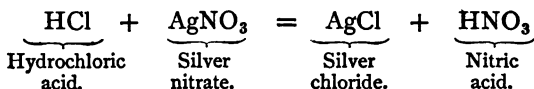
¹ The process given above is that directed by the British Pharmacopœia for the preparation of the pure acid. The crude commercial acid is chiefly obtained as a by-product in the manufacture of 'salt-cake,' or crude *sodium sulphate*. See Part III. p. 283.

Experiment 129.—Mix a few drops of the colourless acid prepared as above with ten or twelve parts of water, and add to the diluted acid a few drops of *silver nitrate* solution. Note that a white precipitate is produced that becomes curdy on shaking. Let the precipitate subside, pour off most of the liquid and then divide the precipitate between two test-tubes.

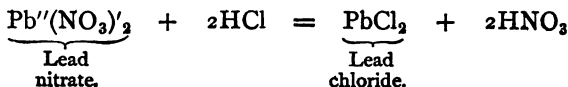
a. To one portion add some moderately strong nitric acid and boil. Note that the precipitate does not dissolve.

b. To the other part add NH_4OH solution; the precipitate soon dissolves completely, and can be reprecipitated when the ammonia is neutralised by nitric acid.

The precipitate possessing these characters is silver chloride, which is formed when silver nitrate is added to free HCl , or to *any soluble chloride* such as ammonium or sodium chlorides—

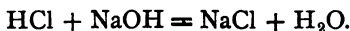


Experiment 130.—Add a few drops of solution of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) to some diluted hydrochloric acid; a white precipitate is obtained if the liquids are not very weak, and the body dissolves to a considerable extent in boiling water and separates out in white crystals on cooling the solution. This body is lead chloride, thus formed—



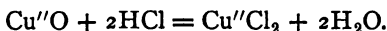
For another useful test of hydrochloric acid or a chloride, see Experiment 137 ; and for the distinction of the acid from free chlorine, see Experiment 147.

Experiment 131.—Dilute some strong hydrochloric acid with water, and add caustic soda until the acid is neutralised, as in Experiment 42. The solution contains sodium chloride, or common salt, and affords crystals of the compound on evaporation—



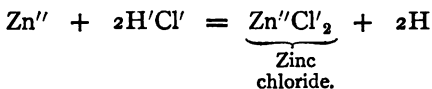
Other metallic hydrates afford corresponding chlorides when used to neutralise the acid.

Experiment 132.—Add some black oxide of copper to a little of the acid in a test-tube ; the oxide dissolves easily and forms a green-coloured solution which contains copper chloride—



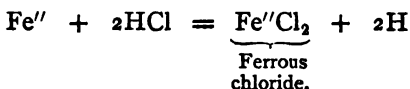
Other basic oxides are acted upon in a similar way by hydrochloric acid, and produce metallic chlorides and water ; but certain peroxides, such as MnO_2 , give chlorine in addition (see Experiment 137).

Experiment 133.—Plunge a strip of zinc into some of the diluted acid in a test-tube. Brisk effervescence takes place, and the gas evolved burns when a flame is applied to the mouth of the tube. The gas is hydrogen resulting from the reaction—



If iron be used instead of zinc, hydrogen is also

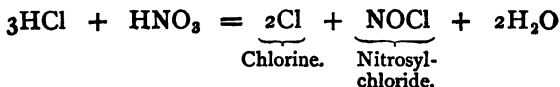
evolved, but ferrous chloride (*ferrum*=iron) is obtained in solution—



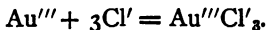
In each case the solid salt can be obtained by evaporation of the solution ; for details, however, see the respective metals in Part III.

Experiment 134.—Take two test-tubes, pour into one 3 c.cs. of strong nitric acid, and into the other 4 c.cs. of strong hydrochloric acid. Put into each acid some pieces of *gold-leaf* and apply heat. Neither acid is able to dissolve the gold, or ‘royal metal’; but on mixing the contents of the test-tubes the particles of gold disappear almost immediately; hence the mixture of acids is called *aqua regia*, because it alone dissolves gold or platinum, which latter is also classed as a noble metal.

When the two *strong* acids react, particularly on heating or long standing, the following products are obtained—



The solution of the gold (or platinum) is due to the action of the *chlorine* on the metal—



The *diluted nitro-hydrochloric acid* (B. P.) is prepared by mixing the strong acids in the above proportion (3 : 4), standing for twenty-four hours to permit nearly

complete change, and then diluting with 25 parts of water.

In order to avoid undue repetition we have hitherto assumed the formula HCl for the gas evolved when sal-ammoniac or when common salt is heated with sulphuric acid. We must now examine this body more closely.

Experiment 135.—We already know that sodium and chlorine are united in common salt. We shall now use the metal to remove chlorine from hydrochloric acid gas. Fill the U tube, fig. 76, with hydrochloric acid by passing a rapid current of the gas through it for some time; then close the stopcock *s* and immediately pour sufficient mercury into the open limb to close the bend *b*, and partially fill the tube as shown. Now adjust the level of mercury by opening the stopcock for an instant, as the gas must be under a little pressure, then mark the position of the mercury in the closed limb and fill up *o* completely with mercury containing some sodium amalgam, prepared as in Experiment 124. Next grasp *o* firmly in the hand, pressing the thumb on the opening and inclining the tube, make the gas go back and forward twice or three times through the mercury containing the sodium, at last transferring all the gas to the closed limb. Now remove the thumb and note that the mercury sinks in *o*; adjust the level of the mercury this time by adding to or removing the metal from *o*, and note that the gas in the closed limb occupies only *half* the volume of the hydro-

FIG. 76.



chloric acid. Fill up *o* with plain mercury, bring a flame near to the jet, and cautiously open *s*—the residual gas rushes out and burns for an instant. This is the hydrogen of which we have now proved hydrochloric acid gas to contain half its volume by Dr. Hofmann's method.

Experiment 136.—Bend a tube in U form as in fig. 77, and introduce some strong colourless solution of hydrochloric acid. Next twist one of the bright terminal wires of a small Grove's battery round a carbon stick of the kind used in the electric lamp, and the second wire round another carbon stick.

FIG. 77.



Now plunge the carbon poles¹ into the acid in the U tube as shown. Gas is evolved at each pole—colourless and abundant at that connected with the zinc side of the battery, less freely at first and coloured from the opposite pole. The colourless gas can be inflamed, and is easily proved to be the hydrogen of the acid; the gas evolved at the positive pole has a distinct greenish-yellow colour, a very irritating smell, and neither burns nor rekindles a match with a glowing tip; if, however, a piece of moistened blue litmus-paper be laid over the mouth of the tube it is soon

¹ Carbon poles must be used, because platinum would be attacked by the chlorine evolved during electrolysis of the acid,

bleached a nearly pure white. This gas is an elementary body and has received the name of *chlorine*,¹ in allusion to its greenish-yellow colour; its symbol is Cl and atomic weight 35.5. The volumes of the two gases evolved during electrolysis are approximately equal when the liquid becomes saturated with chlorine. The specific gravity of chlorine gas, determined as in Experiment 27, is 35.38 ($H = 1$), therefore 1 vol (= 112 c.cs.) weighs 35.38 c.grs.

We know already (see page 63) that the molecular weight of hydrochloric acid gas deduced from its specific gravity is 36.5; and Experiment 135 proved that the molecule, as represented by 2 vols, contains 1 vol, i.e. one atom, of hydrogen, whose weight is 1 c.gr. Now, since $36.5 - 1 = 35.5$, or almost exactly the weight of 1 vol of chlorine, we conclude that the molecule of hydrochloric acid gas consists only of hydrogen and chlorine, and of both chemically combined without condensation. Although this proof is complete, it is well to confirm the conclusion by direct synthesis; before doing so, however, we must endeavour to obtain larger quantities of chlorine in a pure state and study the characters of that element. (For synthesis see page 75.)

CHLORINE—Cl.=35.5. 1 Vol weighs 35.36 c.grs.
 Molecular weight = 71.0.—It is obvious that hydrochloric acid ought to afford an abundant supply of chlorine if we can remove its hydrogen and avoid

¹ From *χλωρός*, in allusion to its colour. Chlorine is only met with in nature in combination, chiefly with sodium in common salt.

presenting at the same time a body that can combine with all the chlorine. Experiment 132 proves to us that a *monoxide* like copper oxide will not suit our purpose, since the metal can unite with all the chlorine displaced by the oxygen, but if we use a peroxide of a metal whose atom requires but two of chlorine to satisfy it, the excess of chlorine should be obtained in the free state. We shall, therefore, make the following experiment with a body of the kind referred to that we have already used, viz., manganese peroxide.

Experiment 137.—Heat a little manganese peroxide (MnO_2) in a test-tube with strong hydrochloric acid; note that a greenish-yellow gas of suffocating odour is evolved which rapidly bleaches moist litmus-paper laid over the mouth of the tube. The gas is chlorine, resulting from the following change—



The manganese chloride (MnCl_2) remains in solution.

Experiment 138.—Mix a little manganese dioxide with common salt and sulphuric acid in a test-tube and note that chlorine is evolved. In this case HCl is first formed by the action of sulphuric acid on common salt, as in Experiment 127; the hydrochloric acid then acts as above on the manganese dioxide.

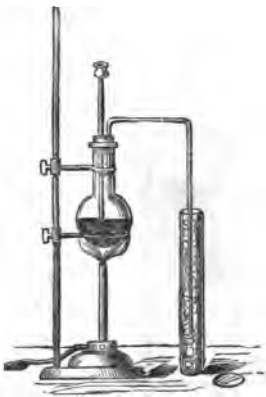
Experiment 139.—Fit a Florence flask with a delivery tube bent twice at right angles, as shown

¹ According to Dumas, MnCl_4 is first formed and then decomposed by heat into free chlorine and manganese dichloride.

in fig. 78. Introduce into the flask about 20 grams of MnO_2 in lumps, and 100 c.cs. of crude but strong hydrochloric acid solution, and apply a *gentle* heat.

Chlorine gas is so much heavier than air¹ that it can be easily collected by displacement of air as shown, the colour of the gas enabling the experimentalist to observe the rate of filling. As each jar fills, remove it and at once cover with a glass plate slightly greased so as to enclose the gas securely. Fill several jars in this manner, and make the following additional experiments, which, as

FIG. 78.



well as the generation of the gas, should be conducted near to a good draught, as the inhalation of chlorine is attended with danger, owing to the irritant action of the gas on the delicate tissues of the lungs.

Experiment 140.—Plunge a burning wax taper into a jar of the gas (see fig. 79). Note that while combustion continues its character alters, for the flame is dull reddish, and much black smoke arises from it, acid fumes being freely produced. The latter

¹ As already stated (page 71), it is 35.5 heavier than hydrogen, and, since air is 14.47 times heavier than hydrogen, it follows that chlorine is almost $2\frac{1}{2}$ times heavier than the same volume of air.

consist chiefly of HCl gas ; and the study of the change leads to the conclusion that the combustion in chlorine is due to the rapid chemical union of the latter with the hydrogen of the wax (a compound of

FIG. 79.



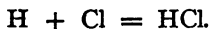
hydrogen, carbon, and a little oxygen), but the carbon does not unite directly with chlorine, and therefore most of it separates, and in the finely-divided state of black smoke or soot. The attraction of hydrogen for chlorine must therefore be very great ; but the following experiment illustrates this important point still more clearly.

Experiment 141.—Moisten a strip of blotting-paper with a few drops of *turpentine* ($\text{C}_{10}\text{H}_{16}$), previously warmed, and, holding the paper by tongs, plunge it into a jar of chlorine. Spontaneous combustion soon takes place, and torrents of black smoke and acid vapour are evolved as before.

Experiment 142.—Take a strong and well-filled jar of chlorine, and another of the same size full of hydrogen gas. Bring them mouth to mouth, and, keeping them close together, invert several times so as to mix thoroughly, then separate and cover with glass plates. The mixture has a yellowish colour. Remove the cover from one of the jars and apply a flame ; an explosion results, and acid fumes of HCl are produced. Bring the second jar, which should be very securely closed by a well-greased ground

glass plate, into diffused daylight, but not into direct sunlight.¹ Note that the yellow colour slowly disappears, and when the contents have become quite colourless, carry the jar to the mercury trough, bring the mouth under the mercury, then remove the plate and note that the gas has not changed in volume, as gas does not escape, neither does mercury enter to any extent. Now pass up a few drops of water by means of a curved pipette, and note that the mercury now rises in the tube and will completely fill it if the original gases were pure and mixed in equal volumes. We have thus effected the synthesis of hydrochloric acid referred to under Experiment 136, and equal volumes have united without change of bulk, and the fact of their union is proved by the solution of the product in a small quantity of water, by which a mere mixture of hydrogen and chlorine would be very slightly affected. Synthesis therefore completely confirms the conclusion drawn from the analytical data.

In these cases



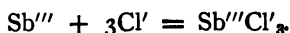
Experiment 143.—Plunge a small piece of dry phosphorus into a jar of Cl, using the long spoon

¹ If the tube were exposed to direct sunlight, almost instant combination of Cl and H would have taken place with explosion. Small and thin glass bulbs are sold ready filled with the mixture of gases, and when exposed to direct sunlight (or to the light emitted by burning magnesium, which is also rich in chemically active violet and ultra-violet rays) the bulb is shattered to fragments, owing to the sudden expansion of the contents by the heat evolved on the combination of the two gases.

for the purpose. The phosphorus soon takes fire in the gas, and produces a mixture of chlorides of phosphorus, PCl_3 and PCl_5 .

Cl can also be made to unite with sulphur, though heat is necessary, but it does not *directly* combine with either oxygen or carbon, though compounds with these elements can be obtained by indirect means.

Experiment 144.—Powder some metallic antimony very finely, and shake the powder into a jar of Cl. As the particles of metal fall through the gas, they burn, evolving much light and producing a most irritating vapour of antimony trichloride—



Chlorine acts upon *arsenic* with equal energy, and, when aided by heat, on all the true metals also, forming therewith chlorides, in which it acts as a single-link or monad element.

Experiment 145.—Write across the printed matter on a piece of newspaper a word or two in black writing ink, and plunge the paper into a jar of Cl. After a short time the writing ink, whose colour is due to gallo-tannate of iron, will be bleached, while the printing ink is unaffected, as the colouring matter of the latter is finely-divided solid carbon, which is not attacked by chlorine. Chlorine is therefore not an universal bleaching agent.

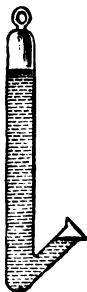
Experiment 146.—Remove a jar of dry gas to the pneumatic trough, and, having allowed some water to enter, close the mouth with the hand and shake up the gas and water ; the hand is drawn in, proving

that absorption has taken place, and on removing the hand under water the latter rises in the jar—therefore Cl is moderately soluble in water. 1 c.c. of water at 15° dissolves 2.368 c.cs. of Cl gas. Such a saturated solution of Cl in water forms the *Liquor Chlorig* of the British Pharmacopœia, and is easily obtained by passing chlorine gas evolved from hydrochloric acid and manganese peroxide through a little water in a wash-bottle (as in fig. 75), and then through distilled water, until gas ceases to be absorbed. A liquid is thus obtained which rapidly bleaches indigo solution, writing ink, &c., and possesses the characteristic odour of the gas. If this solution be cooled by surrounding the bottle that contains it with melting ice, fine white crystals slowly separate which, when drained from the liquid in which they are formed and analysed, are found to consist of $\text{Cl} \cdot 5\text{H}_2\text{O}$. Very slight rise of temperature suffices to decompose this body into chlorine gas and water. Faraday first succeeded in obtaining liquid chlorine by sealing up some of these crystals in a strong glass tube and melting the solid, when two layers of liquid were obtained, the lower and heavier consisting of liquefied chlorine, the lighter of a solution of chlorine in water.

Experiment 147.—Take two test-tubes half full of distilled water, add to one a few drops of the solution of chlorine, and to the other a similar quantity of diluted hydrochloric acid. Now add to each a little silver nitrate solution and note that a similar white precipitate is produced in each case. Repeat the experiment with fresh solutions, but add potassium iodide instead of silver nitrate and note that no

change follows its addition to the hydrochloric acid, while a strong brownish yellow colour is developed in the free chlorine solution, and a black precipitate if the solutions are strong. This change is due to the separation of iodine (see Experiment 159), and serves at once to distinguish free chlorine from pure hydrochloric acid.

FIG. 80.



Experiment 148.—Take a tube of the form shown in fig. 80 and quite fill it with solution of chlorine;¹ now expose it to strong sunlight and observe that bubbles of gas are evolved and collect in the top of the tube, while the liquid gradually loses its yellow colour. Note that the

liquid acquires a strong acid reaction. Since we have only chlorine and water present, and a colourless gas is separated, there is a strong presumption in favour of the gas being oxygen liberated from the water by the superior attraction of chlorine for hydrogen, and in accordance with the equation—



We have already found the acid ; we now test the gas by filling up the little side tube with water, if it be not already quite full, then closing the mouth with a finger and so inclining the tube as to oblige the gas collected to pass into the small limb. Then have a match ready with a glowing tip, remove the finger and

¹ In this experiment the chlorine solution could not be confined in a tube over mercury, as the latter is quickly attacked by free chlorine.

test the gas, when the wood will be rekindled and the presence of oxygen ascertained.

In the absence of light the same change can be effected by passing a mixture of chlorine and steam through a red-hot porcelain tube.¹

The ease with which chlorine decomposes water and sets free the oxygen leads us to enquire whether water plays any part in the bleaching action of free chlorine.

Experiment 149.—Take two perfectly dry stoppered bottles, warm them and fill each with chlorine by displacement of air, but dry the gas before it reaches the bottles by making it slowly bubble through some strong oil of vitriol. Now place in each bottle a strip of red flannel (madder-dyed) previously dried thoroughly by heat, insert the stopper and expose the flannel to the action of the chlorine for half an hour. If proper care was taken to exclude moisture, no material bleaching effect will be observed. Now introduce a few drops of water into one of the bottles, and the colour of the flannel will slowly fade while the dyed stuff in the dry chlorine will retain its colour. In this case, then, the bleaching effect of chlorine is indirect, and due to the powerful action of the *nascent* oxygen (see page 46, and note) derived from water; and similar experiments have shown that in most cases the presence of water is necessary, though we shall meet later on with some exceptions to this rule.

¹ We infer from these facts that chlorine does not tend to unite with oxygen directly, and it is not known to do so; nevertheless many oxygen compounds of the element are obtainable by indirect means (see Experiments 151 *et seq.*)

Chlorine is used in enormous quantities as a bleaching agent, but neither the free gas nor its solution in water are now employed for the purpose, as it is more convenient in practice to liberate the body from 'bleaching lime' and analogous compounds in contact with the materials to be bleached (see Experiments 151 and 152).

Experiment 150.—Introduce a few drops of *ammonium sulphide*—a yellow liquid of very offensive smell—into a bottle and gradually add chlorine water to it with agitation. Note that the unpleasant odour disappears, and the smell of chlorine is not detected unless too much of the latter has been added. In this case, then, the free chlorine acts as a *deodorant*, and it is commonly used for removing unpleasant smells, for which purpose a small quantity is generally sufficient. It is, moreover, believed to act as a *disinfectant*, either by direct corrosion of disease-particles or by its indirect oxidising action, though it is improbable that it usually produces much effect unless employed in large quantities. The most convenient source of chlorine for these purposes is 'bleaching powder,' which affords the gas when a little acid of any kind—vinegar, for example—is added to it (see Experiment 152).

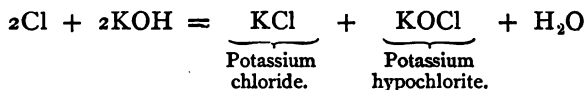
Experiment 151.—Instead of dissolving Cl gas in water, pass it into *cold* solution of potassium hydrate (KOH)¹—the *Liquor Potassæ* (B. P.) answers

¹ If NH₄OH be substituted for KOH in the above experiment, a very different change occurs, for a quantity of *nitrogen* gas is obtained instead of a bleaching solution, thus—



well ; when partially saturated with the gas, stop the current. The solution so obtained is colourless, and smells somewhat like 'bleaching lime.' A few drops of any acid added to a *portion* causes the evolution of chlorine, which is easily recognised by its colour and odour.

The action of Cl on KOH in the cold results in the production of a mixture of potassium chloride and *hypochlorite* in solution, thus—



If into this liquid a piece of madder-dyed wool be stirred, the red colour is not destroyed, as the alkaline hypochlorite does not bleach, but, on the addition of a few drops of dilute hydrochloric or other acid, the colour is discharged. In this case the bleaching agent is chiefly chlorine, resulting from the following reaction—



Potassium hypochlorite is therefore a convenient source of chlorine for bleaching, deodorising, and disinfecting purposes, but in all these cases acidulation is necessary in order to obtain the bleaching or deodorising effect.

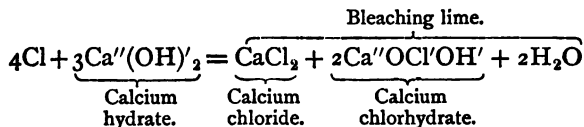
The solution of *chlorinated soda* (B.P.) is obtained by passing Cl gas through solution of sodium car-

This is, in fact, a good method for the preparation of nitrogen gas, but the ammonia must always be present in excess, else there is risk of forming the dangerous chloride of nitrogen (see under Experiment 125).

bonate, when sodium hypochlorite and chloride are formed, and carbon dioxide gas is evolved—



Experiment 152. — If we line the interior of a wide-mouthed bottle with moist slaked lime ($\text{Ca}''(\text{OH})_2$) and pass a slow current of Cl gas into the vessel, the gas is absorbed and combines with the lime, forming the 'bleaching lime' or *chlorinated lime* of the B.P., commonly called 'chloride of lime'¹ :—

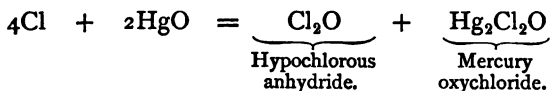


On the large scale the slaked lime is spread in thin layers on shelves in large chambers to which Cl gas is admitted ; the latter is absorbed (just as in the bottle), and 'bleaching lime' obtained as a dull white powder with a feeble odour like chlorine and only partially soluble in water, calcium hydrate separating and impurities in the lime used remaining undissolved. The aqueous solution contains the two calcium salts above named. Bleaching powder or its solution affords HOCl and Cl gas on treatment with any acid (as in the case of KOCl), and is therefore a most convenient source of those bodies for bleaching or deodorising purposes.

The three bleaching salts above referred to are derived from the acid named *hypochlorous acid*, $\text{H}'\text{O}''\text{Cl}'$, which is best obtained by the action of

¹ Its empirical formula is $\text{Ca}_3\text{Cl}_4\text{O}_8\text{H}_6$, which requires 39 per cent of chlorine. The best samples rarely contain more than 38.5 per cent., and always contain more or less calcium chlorate.

its anhydride upon water. The anhydride is prepared by passing dry chlorine gas over dry mercuric oxide,¹ placed in a tube which is cooled. An orange yellow gas results from the action of the Cl on the oxide, and this is the anhydride Cl_2O , which can be easily liquefied by reducing the temperature to -10°C .—



The gas is very explosive, the heat of the hand being often sufficient to decompose it into 2Cl and O ; it is therefore not a safe body for the junior student to prepare. 1 c.c. of water dissolves 20 c.cs. of the gas, and forms solution of hypochlorous acid—



The solution is a powerful bleaching agent.

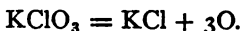
Experiment 153.—Instead of dissolving Cl gas in cold potassium hydrate, pass it into the boiling solution until gas ceases to be absorbed, and allow the liquid to cool. If the potash solution were originally strong, colourless crystalline plates will separate out even before the liquid is quite cold; but if these crystals do not separate on cooling, evaporate the solution down to half its bulk and then cool; collect the crystals deposited on standing and throw them on a suitable filter; pour a small quantity of cold water over them to wash away impurity, repeat the washing if necessary, and then dry. This body,

¹ Prepared by precipitation. See Part III.

when pure, has a cool saline taste and is sparingly soluble in cold water, though easily dissolved with the aid of heat; its name is *potassium chlorate* and its formula KClO_3 , or $\text{K}'-\text{O}''-\text{O}''-\text{O}''-\text{Cl}'$, the body from which we have already prepared oxygen gas (see Experiment 57). In its preparation¹—

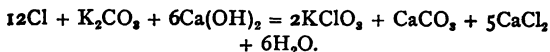


The KCl is a very soluble salt, and therefore remains in solution, while the slightly soluble chlorate crystallises out. When the latter is heated in a test-tube it melts and gives off oxygen, which can be easily recognised by its property of rekindling a match with a glowing tip. Here—



The white residue in the tube consists of potassium chloride, which is easily distinguished from the chlorate by its solution affording a white precipitate of silver chloride (AgCl) when tested with silver nitrate. Potassium chlorate does not give a precipitate with

¹ Instead of pure caustic potash, as above, the B. P. directs Cl gas to be passed through a mixture of solution of potassium carbonate (K_2CO_3) and slaked lime ($\text{Ca}(\text{OH})_2$). In this case—



The mixture is afterwards boiled, then filtered from excess of slaked lime and the chalk (CaCO_3) produced in the process, concentrated by evaporation, and the chlorate crystallised out from the solution.

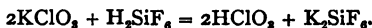
silver nitrate, because silver *chlorate* is a very soluble salt.¹

Experiment 154.—The ease with which the chlorate parts with its oxygen renders it a very powerful oxidising agent ; hence, if a few grains are mixed with a little powdered charcoal and heated on a knife blade, explosive combustion ensues.

Experiment 155.—Pour five or six drops of strong sulphuric acid into a test-tube and add a *very small* crystal of the chlorate, and gently warm ; the mixture becomes yellow, and a yellow gas is evolved which explodes very easily ; hence a loud crackling noise occurs on heating. The gas is a mixture of oxides of chlorine, which decompose into their constituents with explosive violence on gentle heating. This effect is very characteristic of a chlorate, but in applying the test direct the mouth of the tube away from the person.

Experiment 156.—Powder separately a gram or so of potassium chlorate and of dry loaf sugar ; mix the powders on paper with a glass rod, place the

¹ Free chloric acid (HClO_3) is obtained by adding to a saturated solution of potassium chlorate a strong solution of hydrofluosilicic acid (H_2SiF_6 , see page 123) ; the potassium unites with the latter, forming the sparingly soluble salt K_2SiF_6 , which is precipitated, while monobasic chloric acid remains in solution—



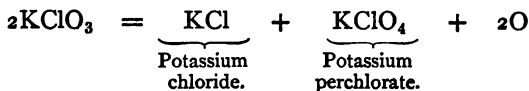
No anhydride of this acid is yet known. We are acquainted with another body, chlorous acid (HClO_2), which is intermediate between hypochlorous and chloric acids, but, like the latter, it is not as yet of any practical importance. The anhydride Cl_2O_3 is known.

mixture on a metal plate and touch the powder with a rod dipped in oil of vitriol; violent combustion ensues, the sugar (a compound of carbon, hydrogen, and oxygen) burning in the available oxygen of the chlorate.

Experiment 157.—Dissolve some of the chlorate in water, add a few drops of indigo solution, and then some strong sulphuric acid. Note that the blue colour is destroyed; as might be anticipated, this bleaching action is due to oxidation.

Experiment 158.—Again heat some potassium chlorate in a tube of hard glass. The salt fuses as before, and oxygen is given off; but, if the heat be steady throughout and not very strong, the contents of the tube become solid, and the evolution of gas ceases. On raising the temperature still higher, gas is again evolved, and in larger quantity than before.

The check just observed occurs when only one-third of the total oxygen has been driven off as gas, and the residue is found to consist of two salts, potassium chloride and potassium perchlorate—a body which is very slightly soluble in cold water, and which is therefore left behind to a great extent when the cooled mass is digested with cold water. The following equation represents the change—



The perchlorate is much less easily decomposed than the chlorate, but ultimately yields up all its oxygen like the chlorate. Hence, in preparing oxy-

gen gas from potassium chlorate, the decomposition takes place in two stages, though we commonly express the change by means of a single equation.

When potassium perchlorate is heated with strong sulphuric acid, an acid distillate is obtained which Roscoe found to contain perchloric acid, HClO_4 —one of the most powerful oxidising agents known, as mere contact with it suffices to kindle paper or wood.¹ No anhydride corresponding to perchloric acid has been obtained.

Neither the acid nor its potassium salts are as yet of any practical importance, but much interest attaches to the former as the highest term of the following series of chlorine acids—

	Acids.	Anhydrides.
Hydrochloric acid . . .	HCl	—
Hypochlorous acid . . .	HClO	Cl_2O
Chlorous acid	HClO_2	Cl_2O_3
Chloric acid	HClO_3	Cl_2O_5 (?)
Perchloric acid	HClO_4	Cl_2O_7 (?)

All these acids contain but one atom of hydrogen within the molecule replaceable by a metal, and are therefore monobasic. They may be regarded as successive oxides of hydrochloric acid (HCl), and their formulæ will be most easily remembered when they are thus viewed. Moreover, the series of bodies may be cited as remarkable illustrations of the *Law of Multiple Proportions*.

¹ The perchlorate does not bleach indigo in presence of sulphuric acid, and is thus easily distinguished from the chlorate.

CHAPTER XVI.

EXPERIMENTS WITH IODINE.

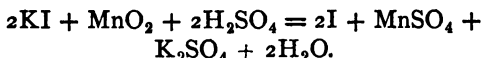
Experiment 159.—Dissolve in water, in a test-tube, a few crystals of the salt potassium iodide (KI), and add a few drops of chlorine water to the liquid. Note that a brown-red colour is immediately produced, and black, heavy particles separate from the liquid if the solutions are strong and sufficient chlorine is added. When the particles have subsided, pour off the coloured liquid, and drain it away as completely as possible from the deposit. Now, without drying, apply a gentle heat to the black substance; a *violet-coloured* vapour is produced, which condenses on the cool upper part of the tube in black, shining metallic-looking scales, the water present volatilising and condensing at the same time. This metal-like substance (or 'metalloid'), characterised by its easy volatility and beautifully coloured vapour, is an element, and is called

IODINE—I' = 127.

The compound with potassium used in this experiment is easily decomposed by chlorine, as we have seen; the latter seizes the metal and forms potassium chloride, while iodine is displaced, thus—



Experiment 180.—Potassium iodide and chloride are obviously analogous bodies ; hence the method already used for the separation of chlorine from its metallic compounds (Experiment 137) might serve for the separation of iodine from the metallic iodide. Mix the latter, or its solution, with some manganese peroxide (MnO_2) in a test-tube, add a few drops of strong sulphuric acid, and apply heat. Violet vapours of iodine are given off, and condense on the sides of the tube as before ; the by-products manganese and potassium sulphates are left—



The reaction is therefore precisely analogous to that in which chlorine is evolved by the action of MnO_2 and H_2SO_4 on common salt.

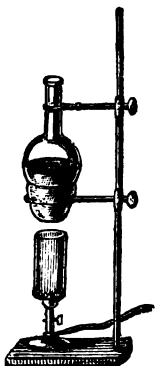
Iodine is widely distributed throughout nature, but in small quantities, and always in combination, though chiefly with potassium, sodium, or magnesium, and sometimes, though rarely, with silver. It is present in many mineral waters, and in sea water ;¹ from the latter the iodides are extracted by various seaweeds, and these, when collected, partially dried, and burned, afford an ash which is termed 'kelp,' and from this ash much of the iodine of commerce is extracted. The process of extraction consists in digesting the kelp with water, which dissolves out a considerable number of soluble salts, including the iodides (and bromides, see page 106) ; the solution

¹ It is also present in small quantity in 'Chili nitre'—sodium nitrate—in cod-liver oil, sponge, &c.

is filtered, evaporated, and the less soluble salts crystallised out and thus separated from the very soluble iodides. The remaining liquor is treated with strong sulphuric acid, and some sulphur is then separated and removed. The acid liquid is next poured into large stills or retorts, manganese dioxide added, and heat applied. Iodine is separated from the iodide as in the above experiment, and distils over ;

it is condensed in a number of tubular receivers, from which it is removed, and, when sufficiently dry, is sent into commerce in a somewhat crude condition. Free iodine and some of its compounds are largely employed in medicine, but it is desirable that the crude element should be purified before it is so used.

FIG. 81.



Experiment 161.—Place a few grams of crude iodine in a crucible, which is to be covered as shown (fig. 81) with a flask containing cold water. A gentle heat

is applied to the crucible, and after a few minutes the flask is removed ; then the small quantity of iodine deposited upon it, with a few whitish needle-shaped crystals of 'iodide of cyanogen,' which usually accompany it, must be scraped off ; the flask is replaced and gentle heat again applied. After some time large crystalline plates of pure iodine will be found attached to the bottom of the flask ; these are to be removed and preserved. If the iodine used in the first instance

were pure, no residue should be left in the crucible at the end of the operation. This process is one of *sublimation*—in which a solid is deposited from a state of vapour.

The specific gravity of pure solid iodine is 4.95 (water = 1).

The element gives off vapour at ordinary temperatures, and it becomes a liquid when heated to 114° C.; it boils at 200° C., and affords its magnificently coloured vapour in abundance, as we have already seen. The specific gravity of the vapour is 125.9, but the atomic weight is slightly higher, or 127.

Experiment 162.—Add to some water in a test tube a few fragments of solid iodine; shake, and allow to stand for some time. The water gradually acquires a brownish-yellow tint, but the proportion ultimately dissolved is very small, as careful experiments have shown that iodine requires nearly 6,000 times its weight of water at mean temperature for solution.

Experiment 163.—Add some litmus to a portion of the dissolved iodine; little or no bleaching is observed, unlike the rapid decoloration that takes place with chlorine.

Experiment 164.—Rub a few pieces of common starch with water in a mortar, and pour the mixture into a capsule. Heat nearly to boiling, with constant stirring, and when the mixture thickens and becomes gelatinous remove the source of heat. Stir the 'made starch' up with warm water until a thin 'mucilage' is obtained, and preserve this for use. Add a few drops of the mucilage to half a test-tube full of

aqueous solution of iodine, and shake ; a beautiful *blue* liquid is obtained, owing to the formation of an ill-defined compound of starch and iodine. This is an excellent and most characteristic test for the free element. Heat the contents of the test tube nearly to boiling, note that the colour *disappears*, but, on cooling, it reappears. Therefore the starch test should always be applied in *cold liquids*.

Experiment 165.—Add a drop or two of starch mucilage to a solution of potassium iodide.¹ No change whatever is observed ; therefore iodine in chemical combination does not give the reaction. Now add to the mixture a drop of chlorine water, or of strong brownish-coloured nitric acid ; iodine is instantly set free and the blue compound formed.

Experiment 166.—Again, put some pieces of iodine into a test-tube with some water ; we already know that very little dissolves, even on long standing ; but now throw in a few crystals of potassium iodide, and observe that on agitating the liquid it becomes of a deep reddish-brown colour, and the solid iodine disappears as the potassium iodide dissolves. The element is therefore much more soluble in potassium iodide solution than in plain water. In this case solution is probably due to the formation of a potassium tri-iodide of the formula KI_3 .

Advantage is taken of this fact in the preparation of the liquor and tincture of iodine of the British Pharmacopœia. In the latter case, however, rectified spirit of wine is the solvent, the solubility of iodine

¹ A very dilute solution.

in alcohol also being increased by the presence of potassium iodide.

Experiment 167.—Add a few drops of *chloroform* to a simple aqueous solution of iodine, and shake. The chloroform subsides on standing, and has a fine purplish colour, as it carries with it the iodine, which is very soluble in it, and is thus easily removed from the water. Iodine is also soluble with ease in ether and in carbon disulphide.

Iodine does not burn in, neither does it directly combine with, free oxygen; but it readily unites with many metals and non-metals.

Experiment 168.—Rub a fragment of iodine with some mercury in a mortar; a reddish powder is first produced, which becomes green if a little more mercury be added and the trituration be continued for a sufficient time.¹ The resulting compound is 'green iodide of mercury'— $\text{Hg''}_2\text{I}'_2$ —thus formed by direct union of the elements.

Experiment 169.—Take a large and wide test-tube—about 10 c.cs. long by 3 c.cs. diameter; introduce a few fragments of iodine, and support the tube in a convenient holder. Apply heat to the tube so as to convert the iodine into vapour, and when the latter half fills the

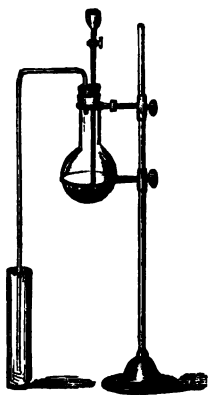
FIG. 82.



¹ The addition of a few drops of alcohol hastens the process by dissolving some of the iodine and thus facilitating chemical action, as in Experiment 6, Part I.

tube plunge into the vapour a very *small* piece of dry phosphorus contained in the deflagrating spoon (fig. 82). The phosphorus takes fire in the iodine

FIG. 83.



vapour and burns for some time ; if the phosphorus be in excess, the colour of the iodine vapour disappears, owing to complete combination of the latter with the phosphorus, an iodide of the latter body being formed—thus, $P + 3I = PI_3$. If, when the tube and its contents have cooled down, a few drops of cold water are allowed to fall upon the dark-coloured body left in the tube, a fuming gas that reddens blue litmus-paper will be given off ; this gas proves on examination to be a compound analogous to

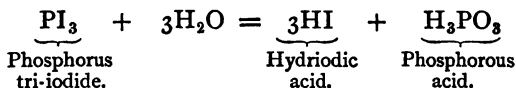
hydrochloric acid, and is termed hydriodic acid—HI—the only known compound of the two elements. We shall now repeat the experiment in such a way as to afford a considerable supply of this gas.

HYDRIODIC ACID = HI. 1 Vol weighs 63·76 c.grs.

Molecular weight = 128.

Experiment 170.—Fit up a flask as shown, fig. 83. Remove the cork and tubes and introduce into it two grams of red or '*amorphous*' phosphorus—not the ordinary waxy variety, as its use in quantity is attended with danger—and 15 grams of powdered

iodine. A very little heat serves to determine the union of the two bodies, and a nearly black mass, consisting chiefly of phosphorus tri-iodide, is formed, as in the last experiment. Insert the cork and support the flask as shown ; then close the stopcock of the funnel and half fill the latter with water. Now turn the stopcock so as to allow the water to fall drop by drop on the iodide in the flask. As each drop of water falls, a colourless and heavy gas is evolved which can be easily collected by passing the straight portion of the delivery-tube into a dry jar ; the air is displaced and a jar full of the dense gas obtained. In this way several jars are to be filled and then covered with glass plates. The hydriodic acid gas thus obtained results from the following reaction—



The phosphorous acid remains behind in the flask. When sufficient gas has been obtained, stop the evolution by turning the stopcock so as to prevent the entrance of more water until a further supply of gas is required. Now turn to the jars of gas.

Experiment 171.—Note that it is colourless, but on removing the plate from a jar it fumes in air ; it has an irritating smell and acid reaction to litmus-paper. Pour some chlorine gas from a tube in which it is generated (by the action of an acid on a little bleaching powder) into the bottle of hydriodic acid gas. Instantly the beautiful violet vapour of free

iodine appears, thus proving the presence of that element in the gas. In this reaction—

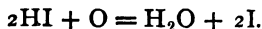


Experiment 172.—Take a large beaker or a tumbler and drop a little strong and brown-coloured nitric acid into it. Then pour from a considerable height hydriodic acid gas from a jar into the tumbler, and note that free iodine quickly appears in the latter. We thus prove that the gas is decomposed by the powerful oxidising agent nitric acid, iodine being liberated; and we also prove that hydriodic acid is a very heavy gas, since it can be easily poured, like a liquid, through air. Its specific gravity is 63.76 ($\text{H} = 1$), 1 vol weighing 63.76 c.grs. Its molecular weight is $63.76 \times 2 = 127.52$, and its formula HI. It is nearly 4.5 times heavier than air.

Experiment 173.—Remove the plate from another jar and immediately bring its mouth under the surface of some water. The latter rapidly rises, proving that HI is very soluble in water.

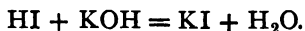
Experiment 174.—A strong solution of HI gas in water is used in medicine to a small extent, and it is easily prepared in the following way. Take a clean jar, introduce some water into it, and allow the delivery tube of the flask (fig. 83) to approach the surface of the water, but *not* to touch the latter. On allowing water to fall slowly from the funnel on the remaining phosphorus tri-iodide, more heavy hydriodic acid gas is evolved, which then falls on the surface of the water and is at once absorbed. If the delivery tube dipped under the surface of the water, absorption

would take place so rapidly that the solution would rush back into the flask. A liquid can be obtained containing 57 per cent. of hydriodic acid, whose specific gravity is 1.9, or almost double that of water. The aqueous solution and the gas are easily decomposed when exposed to air and light, iodine being liberated and water formed—



The iodine is not deposited from the aqueous acid unless decomposition has proceeded very far, but is dissolved by the acid, in which the element is very freely soluble.

Experiment 175.—Pour into a capsule some of the dilute solution of hydriodic acid prepared in the last experiment, and just neutralise with solution of caustic potash; then evaporate the solution until a crust begins to form on the surface of the liquid, and allow to cool. Small cubic crystals separate out which are identical with the *potassium iodide* employed in Experiment 159. The following change takes place on neutralising the hydriodic acid with the alkali—

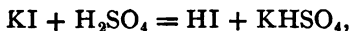


This is the easiest mode of preparing potassium iodide and many other iodides (i.e., by saturating the acid with the hydrate, oxide, or the carbonate of the metal or other basic radicle), but much of the commercial potassium iodide is prepared by the method employed in Experiment 181.

We have already seen that potassium iodide and chloride are analogous bodies, and can afford the

non-metallic radicle by similar treatment. Now we know from Experiments 126, 127 that a chloride affords hydrochloric acid when treated with oil of vitriol ; we have therefore to ascertain whether or not an iodide will afford *hydriodic acid* by similar treatment.

Experiment 176.—Add a few crystals of potassium iodide to a small quantity of strong sulphuric acid contained in a test-tube, and warm. Instead of the colourless hydriodic acid gas we should expect to see evolved, violet vapours of iodine are given off, while a yellow body that can be identified as sulphur separates in the tube, and a suffocating smell is perceived (sulphur dioxide), or an odour of rotten eggs is developed (sulphuretted hydrogen). The sulphur and its compounds separated in this reaction are all products of *deoxidation* of sulphuric acid, and the most probable cause of this is hydriodic acid, which, as we already know, parts easily with its hydrogen, and the latter then available forms water with more or less of the oxygen of the sulphuric acid, and iodine is set free. Hence, though hydriodic acid is doubtless formed according to the equation



it is immediately destroyed in the way just indicated ; but the detailed examination of the reaction must be reserved until we study oil of vitriol.

If this view be correct, we ought to get hydriodic acid gas alone on heating the iodide with a strong acid not so readily reduced or deoxidised as sulphuric acid.

Experiment 177.—Heat a few crystals of the potassium iodide as before, with syrupy *phosphoric*

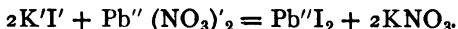
acid,¹ and note that hydriodic gas is evolved and little if any iodine is separated.

Experiment 178.—Add a few drops of silver nitrate to a solution of potassium iodide, and note that a pale yellow precipitate of silver iodide is formed—



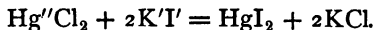
The precipitate is insoluble in dilute nitric acid, and is very slightly soluble in ammonia solution.

Experiment 179.—Add to some dissolved potassium iodide a few drops of lead nitrate solution. Note that a fine bright *yellow* precipitate of lead iodide is at once obtained—



This precipitate is somewhat soluble in boiling water, and separates out on cooling in fine golden spangles.

Experiment 180.—To another portion of the iodide solution add mercuric chloride ($\text{Hg}''\text{Cl}_2$) or 'corrosive sublimate.' By the addition of the first drop, a precipitate, varying in tint from salmon colour to bright scarlet, is obtained, but this dissolves on shaking the liquid. On continuing the addition of the mercury solution, a point is reached at which a scarlet precipitate is obtained which does not dissolve on agitation; this is scarlet mercuric iodide—



This scarlet iodide is easily soluble in excess of potassium iodide, producing a colourless solution, as we have seen; the latter contains a soluble and colourless double iodide of mercury and potassium, $\text{HgI}_2, 2\text{KI}$.

¹ See PHOSPHORUS.

A strongly alkaline solution of this double iodide constitutes *Nessler's test*¹ for ammonia (see page 21).

Hydriodic acid and iodides are thus easily distinguished by the reactions we have learned in the course of these experiments.

Experiment 181.—Warm some caustic potash solution in a test-tube, and add iodine, in small portions at a time, until the liquid assumes a permanent yellowish colour. The element dissolves and forms two salts—one potassium *iodide*, KI, the other potassium *iodate*, KIO₃, thus—



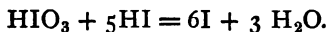
This reaction is precisely similar to that which occurs when chlorine acts on a hot and strong solution of caustic potash, as in Experiment 153, but the iodate cannot be separated from the iodide² quite as easily as can the chlorate from the chloride.

Pour the solution into a small porcelain dish and evaporate to complete dryness. Remove a small portion of the dry residue, which is a mixture of the

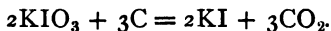
¹ *Nessler's test solution* is thus made—Dissolve 5 grams of potassium iodide in a very small quantity of hot water; add to the liquid a saturated solution of mercuric chloride until the red iodide just ceases to redissolve. Now add 12 grams of caustic potash, previously dissolved in a little water; mix and make up the total volume to 100 cubic centimeters with distilled water; finally add a few drops more of the mercuric chloride solution, allow to stand, and draw off the clear liquid for use; but it must not be filtered through paper. For the action of the test see under MERCURY SALTS, Part III. p. 104.

² The separation is best effected by evaporating the solution to complete dryness and digesting the residue with strong alcohol, which dissolves the iodide but not the iodate.

two iodine salts ; dissolve in some water in a test-tube, add a drop of starch mucilage and then some dilute acetic acid. Note that a blue colour is quickly developed after the addition of the acid, proving that iodine has been set free. In this case the acetic acid displaces hydriodic acid from the iodide, and iodic acid from the iodate, and the two acids thus liberated at once react, producing free iodine and water, thus—



Now return to the dry residue of evaporation ; powder it in the dish and mix with one-fourth its bulk of powdered charcoal. Heat the mixture until it is seen to melt, before which it glows for a short time, owing to the combustion of the charcoal or carbon in the oxygen of the iodate, carbon dioxide gas being formed and evolved, while the iodate is reduced to potassium iodide—



Then allow the mass to cool, add some hot water, and filter from residual charcoal. The solution now contains only potassium iodide (which can be crystallised out), for on adding starch and acetic acid no blue colour is produced.

Most of the potassium iodide of commerce is prepared by the process just followed, and samples of the iodide can be tested for iodate by the method indicated.

Potassium iodate is sometimes used as a test for sulphurous acid (see that body) in acetic and other acids ; the iodate used for this purpose may be separated from

iodide as stated, or, better still, may be specially prepared by the following instructive method directed in the British Pharmacopœia.

Experiment 182.—Heat together in a flask two or three grams of powdered iodine with an equal weight of potassium chlorate and about 10 c.cs. of water acidulated with 5 or 6 drops of strong nitric acid. Chlorine gas is evolved, and the mixture is digested until the colour of the iodine gradually disappears; then boil for a minute or two, pour the liquid out into a capsule, and evaporate to dryness at a gentle heat. The residue consists wholly of potassium iodate, the chlorine and the nitric acid having almost completely disappeared.

This amounts to a replacement of chlorine in potassium chlorate by iodine, thus—

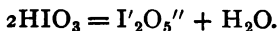


The small amount of nitric acid used facilitates this replacement by liberating small successive quantities of chloric acid, which latter is directly acted upon by iodine.

This decomposition is remarkable, because it proves that chlorine is displaced by iodine from its *oxidised* compound the chlorate, whereas we already know that chlorine easily displaces iodine from the *unoxidised* compound KI. The order of 'affinity' of chlorine and iodine is therefore here determined by the presence or absence of oxygen, and this is found to be generally true.

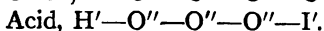
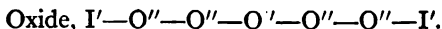
Iodine is converted into iodic acid when boiled in a flask with strong nitric acid, and colourless

crystals of HIO_3 are obtained on evaporation. When these crystals are heated for some time to 170°C . they are decomposed into water and iodine pentoxide (I_2O_5) or iodic anhydride, thus—



The anhydride, when further heated to the temperature of boiling olive oil, is resolved into iodine and oxygen.

Although the formula of iodic anhydride is precisely similar to that of nitric anhydride ($\text{N}^{\vee}_2\text{O}''_5$), it is not necessary to assume that iodine is a five-link or pentad element like nitrogen, or that it is more than a monad or uni-link body, as the constitution of the iodic anhydride and acid can be thus explained on the latter supposition—



The salts of a still higher acid are known, viz. periodic acid— HIO_4 —the analogue of perchloric acid.

CHAPTER XVII.

EXPERIMENTS WITH BROMINE.

BROMINE— $\text{Br}' = 80$.

Experiment 183.—Dissolve in water, in a test-tube, a few crystals of the potassium bromide (KBr), and add a few drops of chlorine water to the liquid. The solution changes to a reddish or brownish colour, but no black substance separates, as in the case of potassium iodide, even on the addition of a larger proportion of chlorine. Boil the liquid, and note that brownish red vapours are given off, and that they have a most unpleasant smell. The body separated by the chemical action of chlorine on the salt employed is an element named *bromine*,¹ in allusion to its smell; its symbol is Br' , and its atomic weight $= 80$. The action of chlorine on the potassium compound is precisely similar to that on the iodide, and is thus represented—

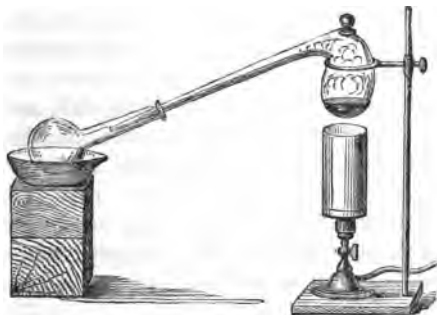


Experiment 184.—Bromine can also be separated from its metallic compounds by manganese dioxide

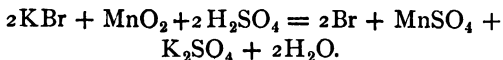
¹ *βρῶμος*, a stench.

and sulphuric acid, as can chlorine and iodine (see Experiments 137 and 160). Mix in a small stoppered retort (fig. 84) a gram or two of potassium bromide with an equal weight of manganese dioxide and sufficient sulphuric acid to make the mixture into a thin paste ; then apply heat, having first passed the beak of the retort into a flask, which latter is cooled by partial immersion in water contained in a capsule, as shown. Brown vapours quickly rise, and are condensed, partly in

FIG. 84.



the neck of the retort and partly in the flask, as a *deep red liquid*, which is to be preserved for experiment. In this case—



Bromine is never met with in the free or uncombined state in nature, its common compounds being the bromides of sodium and potassium ; these are frequently found associated with the iodides, and are

present in kelp, but in much smaller proportion than the iodine compounds. Much of the bromine of commerce is obtained from kelp liquors *after* the iodine has been expelled by the addition of a sufficient amount of manganese dioxide (see page 89). A further quantity of manganese is introduced into the retorts or stills, the receivers changed, and the bromine which distils over collected apart.

Pure bromine is the only non-metallic element known which is liquid at ordinary temperatures. Its colour, as we have seen, is deep brownish-red, and its vapour is also strongly coloured. The specific gravity of the liquid is almost exactly 3 (2.99, water = 1) at 15° C. When the liquid is cooled to — 22° C. it becomes a solid which is hard, brittle, dull, and dark-coloured. On the other hand, when the liquid is heated it boils at 63° C., and affords a vapour whose specific gravity or density is 79.75. 1 vol (112 c.cs. corrected to standard) weighs 79.75 c.grs. Bromine vapour is abundantly given off at ordinary temperatures. The liquid element, as well as its vapour, is powerfully corrosive and poisonous.

Experiment 185.—Shake up a few drops of bromine with some water in a bottle. The water becomes coloured, and the liquid bromine diminishes in volume owing to solution in the water. If the proportion of water to bromine exceeds 33 to 1 by weight, the bromine wholly disappears.¹ Saturated bromine

¹ The solubility of bromine in water is greatly increased by addition of potassium bromide, as in the similar case of iodine and potassium iodide.

water, like chlorine water, when cooled to 0° C. deposits crystals of the hydrate of bromine, $\text{Br}_5\text{H}_2\text{O}$.

Experiment 186.—Pour off some bromine water into a test-tube, and add some litmus solution drop by drop. The colouring matter is bleached, but not nearly so rapidly as by means of chlorine.

Experiment 187.—To another portion of bromine water add some starch mucilage, and note that the latter assumes a *yellow* colour.

Experiment 188.—Dissolve a few small crystals of potassium bromide in water, and add starch mucilage. No change of colour takes place, but on addition of a drop or two of chlorine water the yellow tint appears. Therefore free bromine alone colours the starch, for we already know, from Experiment 183, that bromine is displaced from KBr by Cl .

Experiment 189.—Take a weak solution of potassium *iodide* in a test-tube and add starch mucilage ; then drop in bromine water. Immediately the blue 'iodide of starch' is formed. We already know, from Experiments 159 and 183, that chlorine can liberate both iodine and bromine from their metallic compounds, but this experiment teaches us that bromine can displace iodine ; therefore bromine ranks between chlorine and iodine in attraction for metals and hydrogen as we shall see. Again, its physical condition (liquid) at ordinary temperatures is between that of solid iodine and gaseous chlorine, and its bleaching power is marked, though much less than that of chlorine, while iodine can scarcely be said to bleach at all. Moreover, the atomic weight of bromine is

almost the mean of those of chlorine and iodine, thus—

Chlorine	35'5
Iodine	<u>127'0</u>
	$162'5 \div 2 = 81'25$

Experiment 190.—Add a few drops of chloroform to the aqueous solution of bromine and shake. Note that the chloroform sinks on standing, carrying with it most of the bromine, as evidenced by its colour. Similarly, ether and carbon disulphide can dissolve out and remove free bromine.

Experiment 191.—Add a small quantity of bromine very cautiously to a little mercury in a mortar, and mix as in Experiment 168. Combination takes place, and bromide of mercury is formed.

Experiment 192.—Repeat Experiment 169, using bromine instead of iodine. A similar result is obtained, but the gas given off on treating the iodide of phosphorus with water is the colourless gas hydrobromic acid, HBr—the only known compound of these two elements.

A mixture of hydrogen and bromine vapour may be heated without combination, but in presence of a red-hot spiral of the metal platinum they slowly combine. Hydrobromic acid can also be prepared by a method similar to that given in Experiment 170, but it cannot be obtained on heating potassium bromide with sulphuric acid.

Experiment 193.—Add a few crystals of potassium bromide to a few drops of strong sulphuric acid, and heat. Note that bromine vapour is evolved; the

rest of the phenomena are precisely similar to those observed in the corresponding experiment with potassium iodide, Experiment 176, and the remarks there made apply to the case of the bromide.

Experiment 194.—If, however, syrupy phosphoric acid¹ be used instead of sulphuric acid, hydrobromic acid is easily obtained. Fit up a small flask with a cork and delivery tube, the latter bent twice at right angles, and of sufficient length for one limb to dip to the bottom of a bottle or tube, as in the corresponding experiment with iodine. Place in the flask about 10 grams of potassium bromide, and cover the salt with strong phosphoric acid solution; then apply heat, and note that a colourless gas is evolved which fumes in the air. Collect this gas by downward displacement of air, or over mercury, and test the gas in the same way as hydriodic acid in Experiments 171, 172, and 173.

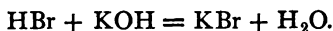
Note that hydrobromic acid gas is a colourless and fuming acid gas, easily decomposed by chlorine or nitric acid with separation of bromine. It is a heavy gas, and has the specific gravity 40·37, and the molecular weight 81, according with the formula HBr . 1 vol (112 c.cs. at 0° C. and 760 m.ms.) weighs 40·37 c.grs. It is easily soluble in water. An aqueous solution of hydrobromic acid is now used in medicine, and is readily prepared by the method just described,² the gas being passed into water until the specific gravity of the solution reaches about 1·1 (water = 1).

¹ See page 96.

² This acid and hydriodic acid can be easily prepared by another method, depending upon the action of free bromine or iodine on sulphuretted hydrogen (see the latter compound).

The aqueous solution of HBr is decomposed by oxidising agents and by light, and bromine is liberated.

Experiment 195.—Neutralise some hydrobromic acid in a capsule with caustic potash, and evaporate as in Experiment 175. Crystals are obtained of potassium bromide—



In this way potassium and other bromides can be prepared from the free acid ; but most of the potassium bromide of commerce is prepared by a method precisely analogous to that employed for the production of KI in Experiment 181 ; the solution must be well boiled in order to ensure the completion of the reaction. The equation expressing the final change is strictly analogous to that given in the case of the iodide, Br' being substituted for I' throughout, potassium bromide resulting and bromate—the analogue of the iodate and chlorate.

Experiment 196.—Add bromine drop by drop to a cold solution of caustic potash or soda until the liquid assumes the orange colour of free bromine ; then remove the latter by the addition of a little more alkali. This treatment is obviously similar to that by which we prepared potassium hypochlorite (Experiment 151), and when the bromine solution is tested in the same way as the hypochlorite it is found to bleach powerfully and to be an energetic oxidiser ;¹ in fact, it contains potassium hypobromite—



¹ For an important use of this solution as an oxidising agent, see Part IV., under *Carbamide, or Urea*.

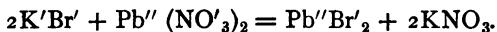
On boiling the solution for some time, or on long standing, it loses its bleaching power, and is then found to contain only bromide and bromate of the alkali metal.

The free acids corresponding to the potassium hypobromite (HBrO) and bromate (HBrO_3) have been obtained, but they are of little importance at present.

Experiment 197.—Add a solution of silver nitrate to one of potassium bromide ; a yellowish or nearly white precipitate of silver bromide is obtained which, like the iodide, is insoluble in dilute nitric acid and is slightly soluble in ammonia—



Experiment 198—To another portion add some lead nitrate solution ; a *white* precipitate is formed—



This reaction therefore serves to distinguish between a bromide and an iodide.

Experiment 199.—Mercuric chloride added to solution of potassium bromide does not give a precipitate. Hydrobromic acid and soluble bromides are therefore easily recognised by the reactions observed in the course of these experiments, and distinguished from chlorides and iodides ; but the points of distinction will be much more clearly noted if the reader throws the statement of reactions into tabular form, showing the action of each test with a chloride, bromide, and iodide.

It has been already pointed out at page 107 that the three elements we have just studied form a

small group of closely related bodies, exhibiting the remarkable gradation in properties there noted, and capable of affording compounds of similar composition. All three seem to act as monads, and unite atom for atom with sodium ; chlorine producing therewith common or sea salt, and iodine and bromine bodies which closely resemble sea salt in many physical characters and chemical relations. Hence this group of three elements is often spoken of as the group of *halogens*,¹ or sea salt producers--the term being used in the limited sense stated.

The most interesting compounds derived from the halogens are the acids formed by the elements, and we now tabulate the formulæ of those known either free or in combination, writing similar bodies on the same horizontal line ; the name of each acid will be found in the foregoing pages, but when no formula is given the acid corresponding is either not known as yet or its identification is unsatisfactory—

Cl'	.	.	Br'	.	.	I'
HCl	.	.	HBr	.	.	HI
HClO	.	.	HBrO	.	.	—
HClO ₂	.	.	—	.	.	—
HClO ₃	.	.	HBrO ₃	.	.	HIO ₃
HClO ₄	.	.	—	.	.	HIO ₄

The chlorine series is complete, as we have already seen (page 87), but there are two gaps in each of the other groups. The missing compounds doubtless can be formed ; hence this is a subject open for investigation by the patient experimentalist.

¹ *Æλς*, sea salt.

CHAPTER XVIII.

EXPERIMENTS WITH HYDROFLUORIC ACID AND SILICON COMPOUNDS.

HYDROFLUORIC ACID = HF. 1 Vol weighs 10 c.grs.¹
Molecular weight = 20.

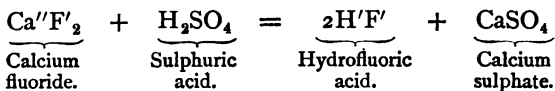
Experiment 200.—Powder some ‘fluor spar’ ($\text{Ca'F}'_2$), a body found native in many localities, but particularly in Derbyshire, and hence often called ‘Derbyshire spar.’ Heat a small quantity of the powdered mineral with strong sulphuric acid in a test-tube, just as in Experiment 127 with common salt, and note that a colourless gas is evolved which has a most irritating smell² and an acid reaction. Moreover, a strip of paper coloured red by tincture of Brazil-wood becomes *yellow* when held in the mouth of the tube and thus distinguishes the body, while the sides of the tube are evidently corroded. The action on the glass tube is best seen by washing it out and then drying it internally, when the corrosion or ‘etching’ of the glass is very apparent.

The corrosive gas thus evolved from fluor spar is termed *hydrofluoric acid*, and is a compound of

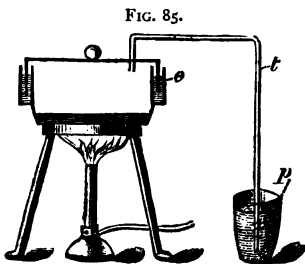
¹ According to the experiments of Dr. Gore of Birmingham; but since the first edition of this part issued, Prof. Mallet of Virginia, U.S., has obtained a much higher value.

² Inhalation of the gas must be carefully avoided, as it is a very powerful irritant.

hydrogen with the monad element FLUORINE, F'. The specific gravity of the gas is 10 ($H = 1$), therefore its molecular weight is 20, or the sum of the atomic weights of fluorine = 19 and hydrogen = 1; hence its formula is HF' .¹ This body is the analogue of hydrochloric acid, HCl , but, unlike the latter, cannot be prepared in any quantity in glass vessels, owing to its corrosive action upon them, and hence is usually generated in vessels of lead or platinum, as it does not act upon either of these metals. The method followed is that employed above, which is explained by the following equation—



Experiment 201.²—This gas, like hydrochloric acid, is easily soluble in water, and its solution is best prepared in the following way. Take a leaden vessel of the form shown in section in fig. 85. Place on the bottom a thin layer of powdered fluor spar and pour over it some strong



¹ The gas can be liquefied if passed into a receiver surrounded by a freezing mixture of ice and salt.

² Instead of making this experiment, which is attended with some danger to the health of the operator, the student may purchase a little of the solution, which is cheap and easily procured.

sulphuric acid ; mix well with a platinum wire, and then put on the cover and pour some sulphuric acid into the channel *c*, in order to make a gas-tight joint. The cover carries a tube, *t*, of lead (or, better still, of platinum), which is soldered or cemented in. This tube conducts the HF gas into some water contained in the platinum crucible *p*, where it is absorbed in large quantity, and a strongly acid liquid ultimately obtained.

The solution of hydrofluoric acid thus prepared can be preserved in vessels of platinum, lead, or gutta-percha, and it is in bottles of the last-named material it is now generally met with in commerce. The liquid acid, often called 'fluoric acid,' is employed in the arts in etching glass.

Experiment 202.—Coat a plate of glass with bees'-wax or paraffin by melting a little of either body and smearing it over the surface of the glass, previously heated. When cold, cut through the protecting layer with the point of a penknife, so as to expose the glass beneath, and in this way trace any desired pattern. Next pour on the engraved plate some solution of hydrofluoric acid, so as to cover the engraved parts. Where the glass has been exposed the acid acts and eats into the surface ; after standing for ten minutes, wash off the acid, dry the plate, and then melt the coating and rub off with a dry cloth. The design will then be found permanently etched into the glass. But the etching thus obtained is *transparent*, and is most easily seen when the glass is breathed upon.

Experiment 203.—Coat a glass plate as before,

and engrave a design through the layer of wax ; but instead of etching the glass with the liquid hydrofluoric acid, expose it to the action of the gaseous acid. For this purpose spread some powdered fluor spar on the bottom of a shallow dish that can be easily beaten

FIG. 86.



out of a piece of stout sheet lead ; moisten the spar with strong oil of vitriol, and immediately cover the dish with the glass plate as shown in fig. 86, the waxed side under. After ten minutes' exposure to the action of the gas, remove the plate and clean off the wax as before. The design will now be found etched into the glass, but the etched surface will be *dull*, and therefore the design will be easily visible on the clear glass.

The character of the etching therefore depends on the condition in which this powerful acid is applied to the glass surface, and a knowledge of the fact enables the glass engraver to obtain some of his best effects.

We have already learned, from Experiments 137, 160, and 184, that when a chloride, an iodide, or a bromide is heated with manganese dioxide and sulphuric acid, the element chlorine, iodine, or bromine appears ; but when a fluoride, such as fluor spar, is similarly treated, the element fluorine is not obtained. It is even doubtful whether the element has been isolated as yet, though a colourless gas, supposed to be fluorine, was obtained by the action of free iodine on excess of silver fluoride, and this gas had no action on perfectly dry glass. Notwithstanding the fact that

so little is known about the free element, chemists are acquainted with large numbers of its compounds, which are very widely diffused, though, with the exceptions of fluor spar and cryolite—a fluoride of aluminum and sodium—they are met with in comparatively small quantities in the solid crust of the earth. Traces of fluorine can be found in the bones of men and other animals, but in largest proportion in the enamel of teeth.

Experiment 204.—Break up a few sheep's teeth and reduce the fragments to as fine a powder as possible ; place in a test-tube, and cover the powder with strong sulphuric acid and heat gently. Test any gas evolved with Brazil-wood paper as in Experiment 200, and after heating the contents of the tube for some time, allow to cool ; wash out the tube, and note that when dried the sides are distinctly etched.

Experiment 205.—Place a small quantity of the hydrofluoric acid solution in a clean leaden dish, and neutralise it with caustic soda solution and slowly evaporate nearly to dryness. A white salt is obtained in small cubic crystals whose composition is represented by the formula NaF ; therefore in form and composition the sodium fluoride as closely resembles common or sea salt as the corresponding iodide and bromide. Hence fluorine is often regarded as a member of the group of halogens, and it is doubtless closely related to them ; but it is not known to form any oxygen compounds whatever, and in this important particular is utterly unlike the true halogens.

We have hitherto assumed the atomic weight for

fluorine stated in the table at page 64, Part I., but we now know that the element has not been isolated ; it is therefore impossible that the usual criteria can have been directly applied—i.e., Avogadro's or Dulong and Petit's. A little consideration will show that the difficulties to be overcome in an exceptional case of this kind are not insuperable, and we can obviously make the first step in the solution of the problem by finding the percentage of calcium in fluor spar, and any one possessing a platinum capsule can make the estimation in the following way.

Experiment 206.—Pick out some pure pieces of fluor spar, reduce them to a *very fine* powder, then, having counterpoised the capsule, weigh into it 100 centigrams (= 1 gram) of the powder. Now place the capsule on a piece of wire gauze supported by the ring of a retort stand, and bring it near to a flue ; pour over the powder a layer of strong and pure sulphuric acid, mix the powder and the acid by means of a small piece of platinum wire, and apply gentle heat. We already know that hydrofluoric acid is evolved in this reaction, and calcium sulphate left behind ; our aim therefore is to drive off all the fluorine in combination with hydrogen, and leave nothing but pure calcium sulphate ; hence, having heated until the mass becomes dry, we cool, add more acid, mix and heat again until vapours of sulphuric acid cease to appear, then cautiously heat to dull redness for ten minutes, allow to cool, and weigh the pure calcium sulphate left, having first removed the platinum stirring wire, from which all adherent particles have been carefully scraped into the capsule.

In an experiment so conducted 100 c.grs. of perfectly pure fluor spar left 174·35 c.grs. of pure calcium sulphate—a body whose formula is well known to be CaSO_4 and the atomic weights of its constituents thoroughly ascertained; the weight of calcium in it is therefore easily calculated thus:—The molecular weight of the sulphate is

$$40 + 32 + (16 \times 4) = 136.$$

$$\text{Then } 136 : 174\cdot35 \therefore 40 : x - (x = 51\cdot27).$$

The answer 51·27 is the weight of calcium contained in 100 c.grs. of fluor spar, and the difference (100—51·27) must be the weight of fluorine *if the spar contains only the two elements*; hence 100 parts of fluor spar contain—

Calcium	51·27
Fluorine	48·73
						<hr/> 100·00

The next step is to find the weight of fluorine combined with one atom—i.e., 40 parts of calcium. This is easily found by the proportion—

$$51\cdot27 : 40 \therefore 48\cdot73 : x - (x = 38\cdot01).$$

The weight of fluorine, combined with one atom of diad calcium, is therefore as nearly as possible 38; if fluorine be a diad element this number is its atomic weight, but if a monad, then $38 \div 2 = 19$ must be its atomic weight. In order to decide between these numbers it is necessary to know the specific gravity of some gaseous fluorine compound, and the most suitable for the purpose is its hydrogen compound,

hydrofluoric acid. Now if the specific gravity of this gas, as already stated, is 10 ($H=1$), 20 is its molecular weight—that is to say, exactly $1+19$; therefore fluorine is a monad element, with an atomic weight=19.

There is one assumption involved in this process—namely, that the matter we call fluorine is really an element; but in the absence of evidence to the contrary the proof is complete, and, even if our fluorine should hereafter be shown to be a compound radicle, our determination of the combining weight of that radicle will not be affected.

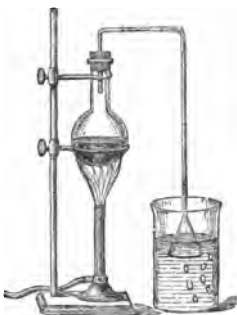
The mode of solving the problem we have adopted is obviously one of very general application, for if we can thus indirectly determine the atomic weight of an element not known in the free state, it is *a fortiori* possible to do so in the case of an element which has been distinctly isolated. We shall presently meet with other illustrations of the use of the indirect method.

SILICON TETRAFLUORIDE, $Si^ivF^I_4$. 1 Vol of gas weighs 52 c.grs. Molecular weight = 104.—We have already learned that hydrofluoric acid corrodes glass in such a way as to lead to the conclusion that matter is removed from the glass even when the gaseous acid acts upon it. It would appear, then, that a portion of the material is removed in the gaseous form. We shall now make an experiment under the most favourable conditions for securing the full action of hydrofluoric acid on glass.

Experiment 207.—Crush some pieces of broken glass bottles, &c., and reduce to a rather fine powder

in a mortar. Mix the powdered glass with an equal weight of fluor spar, also in fine powder. Introduce the mixture into a Florence flask provided with a delivery tube, as in fig. 87, but at first without the funnel shown, and pour in sufficient oil of vitriol to cover the powder with a good layer of acid. We know already, from Experiment 200, that HF gas will be produced by the action of the sulphuric acid on the fluor spar, but at the moment of its liberation it will have the opportunity of acting freely on the glass. Action evidently commences before the application of heat to the flask; but on gently warming, effervescence takes

FIG. 87.



place, and a colourless gas issues from the mouth of the flask which is observed to fume in the air; and a glass rod moistened with water, when held over the mouth of the flask, becomes quickly coated with a white film, which can be easily rubbed off the rod.

Now insert the cork carrying the delivery tube in the flask, and conduct the gas down to the bottom of a *dry* jar. The sides of the latter are evidently not corroded by the gas, and when the latter fills the jar—as evidenced by fuming at the mouth—a taper let down into the gas is extinguished without kindling it.

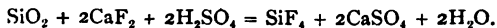
A jar full of gas, when removed and shaken with a small quantity of water, produces a very turbid

mixture, which is acid to test-paper. No such turbidity is caused when hydrofluoric acid gas is passed into water. As a solid results from the action of water on the gas, there is evidently some risk of the narrow delivery tube becoming choked if we place it directly in some water. We can avoid any danger arising from this cause by connecting a small glass funnel with the end of the delivery tube, as shown, by means of a flexible tube; the gas may then be allowed to issue from the wide mouth of the funnel into water contained in the beaker *b*. The bubbles of gas in passing through the water become coated with a somewhat gelatinous layer, and if the gas be passed for some time the liquid becomes quite thick. When the evolution of gas ceases, remove the delivery tube and funnel from *b*.

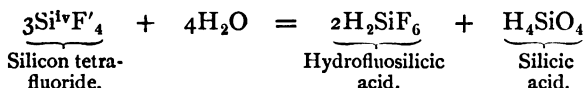
The gas obtained in this experiment is termed silicon tetrafluoride, and its formula is $\text{Si}^{\text{IV}}\text{F}_4$.¹ 1 vol weighs 52 c.grs., therefore its molecular weight is 104. The fluorine it contains is evidently derived from the hydrofluoric acid, and the silicon from the glass, of which it is an essential constituent. The etching of glass by hydrofluoric acid is therefore due to the removal of this silicon by fluorine, owing to the powerful attraction existing between these elements.

Experiment 208.—Filter the turbid mixture obtained by the action of water on the gaseous silicon

¹ The same gas is formed when quartz sand (SiO_2), fluor spar, and sulphuric acid are heated together. In this case the change is represented by the equation—



tetrafluoride, and note that the clear liquid that passes through has a strong acid reaction, while a semi-gelatinous body is left on the filter. The liquid contains a soluble acid—hydrofluosilicic acid, H_2SiF_6 —and the insoluble gelatinous body essentially consists of another acid—silicic acid, H_4SiO_4 . The action of water on silicon tetrafluoride is represented by the following equation—



Preserve the silicic acid on the filter for further examination, and test the solution of hydrofluosilicic acid¹ in the following way.

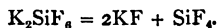
Experiment 209.—*a.* To a portion add solution of barium nitrate— $\text{Ba}''(\text{NO}_3)_2$ —and note that a white precipitate of $\text{Ba}''\text{SiF}_6$ is formed, which is *not* dissolved even on heating with some hydrochloric acid.

b. To another portion add a strong solution of potassium nitrate; note that a nearly transparent precipitate forms of K_2SiF_6 .² Sodium nitrate does not give a precipitate with the acid, therefore the latter is used in analysis to distinguish between soluble compounds of potassium and sodium.

c. Collect some of the potassium silicofluoride

¹ It is only known in solution.

² Potassium silicofluoride and the corresponding salts of other metals, when heated strongly, afford silicon tetrafluoride gas and metallic fluoride—



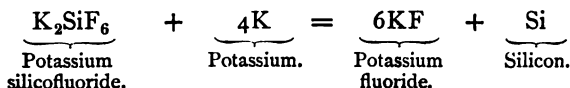
prepared as in *b*, dry it, and add it to a few drops of oil of vitriol contained in a test-tube, and warm gently. Note that gas is evolved, and a moistened glass rod, when held in the mouth of the tube, is coated with a white film. When the contents of the tube have cooled down and it is washed out and dried, the sides of the glass are seen to be corroded. Therefore silicon tetrafluoride and hydrofluoric acid have resulted from the action of the oil of vitriol on the salt. The following equation expresses this change—



SILICON = Si^{4v} . *Atomic weight* = 28.—We already know that fluorine removes from ordinary glass one of its constituents and forms therewith gaseous silicon tetrafluoride ; the question now arises how we can separate this silicon from its compound with fluorine. The fact that fluorine forms a powerful acid with hydrogen leads to the conclusion that it should be removed from its silicon compound by the action of any metal for which it possesses a great attraction. Amongst the metals, potassium is found to be most active in removing the fluorine ; but instead of acting on silicon tetrafluoride gas the solid potassium silicofluoride can be more conveniently employed.

Experiment 210.—Mix some dry and finely-powdered potassium silicofluoride in a test tube of hard glass with about three-fourths of its weight of metallic potassium, carefully cleaned and cut in small pieces. Apply gentle heat to the tube ; the potassium

melts and quickly acts upon the silicofluoride ; then increase the heat to redness, allow to cool completely, and break the end of the tube, throwing the fragments into cold water. After stirring well, pour off the turbid liquid through a filter, but the heavier particles of glass must be left behind. Wash all brownish matter away from the glass and on to the filter ; then wash the latter with cold water, and finally with boiling water, until all soluble matter is removed. Then dry the filter and carefully remove from its surface a dull brown powder. This is *silicon*, separated from the silicofluoride by potassium, according to the equation—



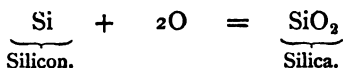
Silicon as thus obtained is insoluble in water and in nitric or sulphuric acids, but soluble in hydrofluoric acid, as might be anticipated. This form of silicon does not exhibit any trace of crystalline structure, and is therefore spoken of as the *amorphous*¹ element. Two other forms of silicon are known which are crystalline, the *graphitoid* and *adamantine*.

Silicon can be fused when strongly heated in an atmosphere of hydrogen, but when heated in air it oxidises easily.

Experiment 211.—Place a little amorphous silicon on a slip of platinum foil and heat to full redness over the Bunsen gas flame ; the element glows, and is

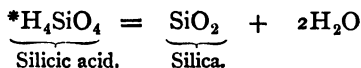
¹ Gr. α , without ; and $\mu\rho\rho\eta$, shape.

superficially converted into a white body, which is a dioxide of silicon, SiO_2 , commonly called *silica*—

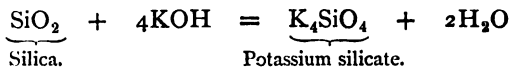


This silicon dioxide, or silica, is the anhydride of an acid that we have already met with—the silicic acid obtained in Experiment 208.

Experiment 212.—Place some of the gelatinous body obtained in Experiment 208, and which contains silicic acid, in a porcelain crucible, and gently heat ; water is driven off, and, after heating to redness, a white powder is left which is identical with the silica prepared by direct synthesis—



Silica as thus obtained is a white mobile powder, of specific gravity nearly = 2 (water = 1). It does not dissolve in or unite with water or any acid save hydrofluoric acid ; but it is soluble in a hot and strong solution of caustic potash or soda, and produces an alkaline *silicate*—



Silica occurs abundantly in the solid crust of the earth, but silicon is never met with in the free state. We meet with the former under the fine crystalline forms of quartz and rock crystal, and their variously-

* By partial dehydration a dibasic acid, H_2SiO_3 , is formed. Most of the mineral silicates are salts of one or other of these acids.

coloured varieties; ¹ amorphous, as agate, bloodstone, flint, &c., and, as hydrated silica, in the common and the precious opal. Sea and river sand also consist for the most part of fine hard granules or crystalline fragments of silica; and sandstone rock is chiefly composed of particles of silica adherent by mineral cement.

Experiment 213.—Obtain a piece of coarse-grained granite. Examine it closely, and observe that it is evidently a mixture of three distinct bodies—*a*, a glassy, colourless, and transparent mineral (this is silica in the form of quartz or rock crystal); *b*, a grey or a reddish-coloured opaque body, having a somewhat greasy lustre (this is *felspar*); and *c*, a mineral that occurs in strongly-reflecting plates, which can be easily split up (this is *mica*). Collect and preserve each mineral separately. The composition of each is represented by the formula given below—

Quartz	SiO_2
Felspar (silicate of potassium and aluminum)	$\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$
Mica, white, (silicate of potas- sium and aluminum)	$\text{K}_4\text{Al}_4\text{Si}_5\text{O}_{18}$

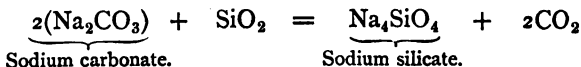
Therefore granite is a mechanical mixture ² of three chemical compounds—quartz, or silica, and the two distinct *silicates*, felspar and mica.

¹ Common amethyst, cairngorm, &c. are but crystallised silica coloured by metallic oxides.

² A piece of granite may be used as an excellent illustration of the difference between a mechanical mixture and a chemical compound.

Very large numbers of analogous silicates are found in large quantities in the solid crust of the earth, and common clay consists for the most part of an impure silicate of aluminum. Therefore silicon, in one form or another, is one of the most widely diffused of the elements. Solid silicates can easily be prepared artificially, and of these the varieties of glass are the most important.

Experiment 214.—Mix one part of the fine ‘silver sand’ used by gardeners, which is nearly pure silica, with three and a half times its weight of dried sodium carbonate.¹ Introduce the mixture into a common fireclay (Hessian) crucible, and make a bed for the latter in a good fire; allow the crucible to heat gradually lest it should crack, and then urge the fire by a bellows until the contents of the crucible are quite liquid; at first gas is freely evolved, but after a time the quiet fusion of the whole mass is complete, and it may be poured out on an iron plate and allowed to cool. The product is a ‘soluble glass,’ or sodium silicate, formed in the following reaction—



When the glass is powdered and warmed with five or six times its weight of water in a test tube, most of it dissolves, if the fusion has been thoroughly effected, and the filtered liquid contains the sodium silicate.

Experiment 215.—The solution is highly alkaline to test-paper; now add to it an excess of hydrochloric

¹ Obtained by heating to low redness, in an iron ladle, common ‘washing soda’—the crystallised carbonate.

acid ; gelatinous silicic acid separates,¹ being displaced by the stronger acid, while sodium chloride is formed and remains in solution—



Silica also affords a soluble glass with potassium. If in either case the proportion of alkaline carbonate to silica be much reduced, the solubility of the silicate in water is lessened, as *acid* silicates are thus obtained which are in all cases less soluble than those completely saturated with alkali or base. Again, calcium, aluminum, and lead silicates are insoluble in water even when basic, though they are more or less decomposed by acids ; but when fused with alkaline silicates the mixtures are not acted upon by water or acids. Ordinary glass is such a mixture of silicates. *Window glass* consists essentially of a mixture of sodium, calcium, and aluminum silicates ; *plate glass* of sodium, potassium, and calcium silicates ; *Bohemian hard glass* of potassium and calcium silicates ; and *flint glass* of potassium and *lead* silicates. *Black bottle-glass* contains iron silicate in addition to the alkaline and calcium compounds.

In the manufacture of glass, sand, alkaline carbonate, chalk (to supply calcium), or red lead in the case of flint glass, are mixed with a variable proportion of broken glass. The mixture, after gentle heating

¹ If the solution be dilute, very little silicic acid separates, and if the liquid be placed on a dialyser (see Part III. p. 190) the sodium chloride and excess of hydrochloric acid diffuse away and leave behind a liquid which contains silicic acid in the *colloid* condition.

for some time, or 'fritting,' is introduced into large fire-clay pots or crucibles, and several of these are arranged in a furnace, which latter is usually of circular form. The mixture is then fused, and when freed from scum of less fusible impurities, the glass is withdrawn and blown or moulded into the desired forms, and the articles are then allowed to cool very slowly in a chamber termed the *annealing* oven.

Glass which has been suddenly cooled tends to fly in pieces on any slight injury or on receiving a shock, as the particles are in a state of tension ; hence the importance of slowly cooling or annealing glass required for ordinary use, as the particles are given time to adjust themselves to the change of temperature. This difference between annealed and unannealed glass is well illustrated by an old toy.

Experiment 216.—Obtain a 'Prince Rupert's drop' (which is a tear of glass obtained by allowing some of the molten material to fall into water and suddenly solidify) and place it carefully in a stout glass tumbler ; now nip the thin end with pincers, and the whole 'drop' will be instantly shattered to atoms with a little explosion. A piece of ordinary annealed glass rod treated in the same way breaks, but does not crumble.

The composition of the fluoride of silicon, SiF_4 , is sufficient evidence of the tetratomicity of silicon, since we have already found fluorine to be a monad, and the conclusion is confirmed by the examination of compounds of silicon with other monads. The formulæ of these bodies are given in the annexed table ; but their preparation is too difficult to be

attempted by a beginner, and therefore is not described—

Name	Condition at 15° C.	Weight in c.grs. of 1 vol of gas or vapour	Molecular weight	Formula
Silicon Hydride	A gas	16 c.grs.	32	SiH ₄
„ Chloride	A liquid	85 „	170	SiCl ₄
„ Bromide	A liquid	174 „	348	SiBr ₄
„ Fluoride	A gas	52 „	104	SiF ₄

If from the molecular weight of each compound, as determined in accordance with Avogadro's law, we deduct the weight of four atoms of the monad element present, the constant residue 28 is obtained as the weight of silicon in one molecule of each compound. Thus in the case of the

Hydride	32 - 4 (weight of 4 atoms of H)	= 28
Chloride	170 - 142 („ „ Cl)	= 28
Bromide	348 - 320 („ „ Br)	= 28
Fluoride	104 - 76 („ „ F)	= 28

As 28 parts of silicon is the *least weight* of the element that we meet with in the molecule of any chemical compound whose composition can be accurately determined, we conclude that 28 is the atomic weight of the element. Now this mode of arriving at the atomic weight of an element is of special importance in the case of silicon, because the free element cannot be converted into vapour and have its specific gravity taken in that condition ; therefore Avogadro's principle cannot be directly applied ; and the weight of it that

contains the same quantity of heat at 100° C. as 108 c.grs. of pure silver is 33 c.grs. But by the examination of the above compounds we have distinct proof that the atomic weight of silicon cannot be *more* than 28, and we conclude that the latter is the correct value, and that silicon is an exception to Dulong and Petit's law.

CHAPTER XIX.

EXPERIMENTS WITH VARIETIES OF CARBON.

CARBON = C^{12} . *Atomic weight* = 12.

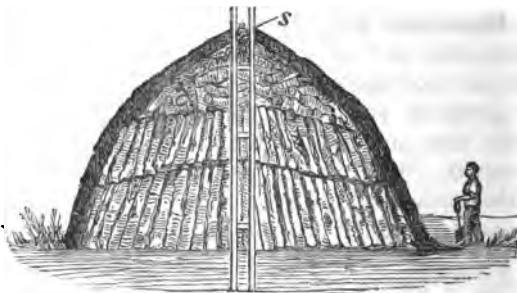
Experiment 217.—Heat a small piece of wood in a long tube of hard glass closed at one end. Note that the wood becomes discoloured, and that vapours are given off which partially condense on the sides of the tube, and an unpleasant penetrating odour is perceived. When a moist piece of blue litmus is held in the issuing vapour it is reddened, indicating that *acid* products result from the decomposition of wood by heat.¹ On continuing the heat a black coal-like residue is left in the tube, having the form of the original wood, but completely charred by heat. This is *wood charcoal*, and consists almost wholly of the element CARBON. If air had free access to the charcoal when hot, the latter would burn away and leave only a small quantity of a white ash; hence, in the preparation of charcoal, air is as far as possible excluded.

On the large scale, wood charcoal is usually obtained in the following way. Faggots of wood are stacked in heaps, as shown fig. 88, but so that air-

¹ This process is spoken of as one of *destructive distillation*.

passages traverse the mass, terminating in a central shaft, *s*. The whole is then covered with damp sods, but a hole is left at the top for the escape of smoke ; the wood is then kindled at several points round the base of the cone, and imperfect combustion slowly proceeds, the air-supply being so regulated by adding or removing sods that the necessary temperature may be maintained to secure complete decomposition of the wood, while the minimum amount of charcoal is

FIG. 88.



wasted. When the process is judged to be complete, the mass is completely covered with earth, and, when cold, the stack is opened and the charcoal removed. In this case, all the volatile products are wasted, and only about one-fourth of the weight of the original wood remains as charcoal.¹

Experiment 218.—Heat a piece of bone in a tube,

¹ When wood is distilled in large iron retorts, charcoal is also obtained ; but the volatile products are also collected, and the most important of these are acetic acid—the acid of vinegar—and wood spirit, or methylic alcohol (see Part IV.)

just as the wood was heated in the last experiment, and note that while charring occurs, as in the case of wood, the vapours evolved are *alkaline* to test-paper, and have a very disagreeable ammoniacal smell. This difference is due to the presence of nitrogen in the bony tissue, which is only found in that of wood in very minute proportions. The charred residue retains the form of the bone heated, and constitutes *animal charcoal*, or bone black.

Experiment 219.—Take a small piece of wood charcoal and another of as nearly as possible the same size of bone charcoal, and place each on a slip of platinum foil and heat until all black coloured matter has disappeared. Note that the wood charcoal leaves but a small proportion of light white ash, which can be easily crumbled between the fingers. On the other hand, the animal charcoal seems but to change its colour, as the nearly white residue is as hard as the charcoal, retains its form, and does not easily crumble when pressed. This ‘ash’ consists almost wholly of calcium phosphate, a body which occurs only in minute quantity in the ash of wood. Introduce the ash from bone charcoal into a test-tube, and heat with some hydrochloric acid. Note that the calcium phosphate dissolves.

Experiment 220.—Boil with hydrochloric acid some of the bone black prepared in Experiment 218, and previously powdered; when cool, throw on a filter, and wash the black residue on the paper until the liquid that passes through ceases to give an acid reaction to test-paper. When a little of the black residue is dried and heated on platinum foil, it burns

away, leaving but a minute trace of ash. Thus, by treatment with hydrochloric acid, the calcium phosphate is dissolved and removed from the black body with which it was previously mixed. The latter is the nearly pure element carbon. This experiment illustrates the process directed by the British Pharmacopœia for the preparation of purified animal charcoal. When any kind of charcoal is added to molten iron the latter dissolves a certain small proportion of carbon, and on slow cooling most of the latter previously held in solution separates out in plates. When the iron is treated with hydrochloric acid, the metal dissolves and leaves these plates of carbon behind. The carbon thus obtained is identical in all essential characters with the *plumbago*, or 'black lead,' which is found native at many places in the earth—viz., Borrodale in Cumberland, Ceylon, St. John's in New Brunswick, in Siberia, and in the United States of America. This form of the element is often termed *graphite*, since it is the material employed in the production of the ordinary pencils used in writing. In the production of these useful articles the native graphite, after partial purification, is powdered and compressed into thin plates, which latter are cut into the well-known long prisms which, encased in wood, constitute the cedar pencils commonly used.

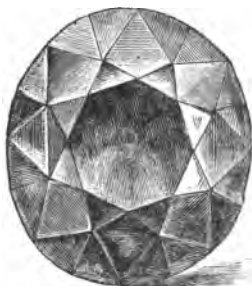
We may here anticipate evidence we shall presently obtain relating to the composition of the beautiful mineral *diamond* by stating that it is but another form of carbon. Neither charcoal nor plumbago have as yet been converted into this form, though it has been recently stated that some of the com-

pounds of carbon can be made to afford the element in the state of diamond. All our supplies are at present drawn from native sources, as the diamond is always found in alluvial washings or in granular quartz rock. The most celebrated diamond fields are those of Golconda in India, Borneo, Brazil, and the Cape of Good Hope. In all these localities discoloured or even perfectly black crystals are obtained ; but the smoky or almost black stones, technically termed *boart*, that are useless in jewellery are of great value in glass cutting, rock boring, &c., and can be easily purchased at a very low price. One of these cheap diamonds will answer well for the experimental comparison we propose to institute between the three chief forms of the element carbon—viz, charcoal, black-lead or plumbago (derived from a ‘lead pencil’), and diamond.

Before entering on this comparison, however, it may be interesting to point out that diamonds have for ages been eagerly sought for, partly on account of their beauty and rarity, but in part because they, as well as other ‘precious stones,’ were supposed to possess miraculous powers. Thus to the diamond Serapius ascribes the power of driving away almost all diseases, and of making men courageous and magnanimous ! The natives of India regard the gem as a preservative against lightning, and imagine that when taken into the mouth in the form of powder it makes the teeth fall out ! The value attached to large diamonds free from defects and of great brilliancy is so great that they have not inaptly been described as the ‘essence of money ;’ thus the largest gem, according

to Mr. Emanuel, from whose interesting work¹ we quote, belongs to the Rajah of Mattam, in Borneo. It is of pure water, weighs about $2\frac{1}{2}$ ounces troy, and is of pear shape. It was found in 1760, at Landak,

FIG. 89.



in Borneo, and has been the cause of a sanguinary war. The Dutch Governor of Batavia offered the Rajah *two gunboats*, with stores and ammunition complete, and 50,000*l.* for it; but the offer was refused. Our own Koh-i-noor (Hill of Light) is believed to have originally weighed 793 carats (1

carat = 4 grains troy), in which case its value would be something over half a million sterling; but by repeated and sometimes careless cutting it has been reduced to but 106 carats (or about $\frac{3}{4}$ ounce), and is now valued at 120,000*l.* Fig. 89 represents the actual size and appearance of this diamond.

Experiment 221.—Take a piece of charcoal, another of black-lead, and a small diamond or ‘boart,’ and rub each along a piece of paper. The *charcoal* gives a black streak on the paper, and this form of carbon is used in artists’ *crayons*. The black-lead or plumbago form gives a *lead* grey streak, and this is the variety used for pencils and, in its crudest form, for polishing grates. The *diamond* does not

¹ *Diamonds and Precious Stones*, by H. Emanuel, F.R.G.S.

give a coloured streak. Note the difference in colour between the mass of black and opaque charcoal, leaden metal-like plumbago, and nearly colourless and transparent diamond. Moreover, the charcoal is *amorphous* in the sense that it does not exhibit the slightest trace of crystalline form, whereas the plumbago or graphite occurs in six-sided plates or prisms, and diamonds usually in a form with curved faces, often resembling fig. 90.

FIG. 90.



Experiment 222.—Press the thumb nail upon the surface of the charcoal ; it is easily indented, and therefore its hardness is low.

Plumbago is also marked by the nail, but less easily than charcoal. Though rather harder than the latter, the peculiar greasy surface of the plumbago particles renders it an excellent *lubricator* when used instead of oil between the working parts of machinery.

The diamond when pressed with the nail is not marked, nor is it scratched by the hardest steel file, or by anything save its own dust. It is the hardest¹ body known, and is used in glass-cutting, rock-boring, and for all purposes in which great power of resisting

¹ The relative 'hardness' or degree of cohesion of the particles of a body is commonly measured on a scale of 10, and the following typical minerals were used by Mohs as standards :—Talc = 1°, rock salt = 2°, calc spar = 3°, fluor spar = 4°, apatite = 5°, felspar = 6°, quartz = 7°, topaz = 8°, corundum = 9°, diamond = 10°. If a body be less easily scratched than calc spar, but more easily than fluor spar, its hardness is between 3° and 4°, and so on.

abrasion is required. Although the diamond resists friction better than any other body, it can be broken into fragments by a sharp blow with a steel hammer.

Experiment 223.—Examine with a magnifying glass the three forms of carbon. Note that the charcoal appears honeycombed—so *porous* is it, while fewer pores are observable in the plumbago, and the diamond is scarcely porous, though under a high power it usually exhibits a few minute cavities—Sir David Brewster's cavities—which generally contain liquid.

Throw the three specimens into water ; the charcoal floats, but the other varieties sink. If, however, the vessel be placed under the receiver of an air-pump, the air contained in the pores expands under diminished pressure, in accordance with Boyle's or Mariotte's law, and the charcoal begins to sink ; on allowing air to re-enter the receiver, water enters the pores previously occupied by air, and the lump rapidly sinks. Thus ordinary charcoal appears to be of lower specific gravity than water, but it is merely buoyed up by enclosed air. When the latter is removed it is found to be heavier than its own volume of water, the ratios, or specific gravities of the three forms of carbon and water being—

Water	1.0
Charcoal (wood)	1.3 to 1.8	
Plumbago	2.3	
Diamond	3.5	

There is therefore a wide and real difference in density between the three forms of carbon ; but

not only is the specific gravity of diamond greater than that of its congeners, but it is greater than that of any other gems the diamond can be confounded with. The latter can be completely distinguished by its high *gravity*, great *hardness*, and insolubility in *all acids*, but especially in hydrofluoric acid, which easily attacks rock crystal or glass.¹

Experiment 224.—Interpose in succession the three forms of carbon between the wires in the arrangement shown in fig. 24, and in such a manner that the specimen serves to connect the wires. Note that neither charcoal² nor diamond convey the current in any sensible degree, while the plumbago conducts electricity almost as easily as a metal.

Advantage is taken of the electric conductivity of plumbago in electrotyping. A wax, gutta-percha, or other non-conducting mould of a medal or other object is brushed over with plumbago and then immersed in solution of copper sulphate and connected with the negative pole of a simple cell, such as that employed in Experiment 5, while a plate of copper forms the other or positive pole. Metallic copper is deposited on the plumbago-coated surface, and an electrotype reproduction of the original is thus obtained in copper ; but this deposition would not take

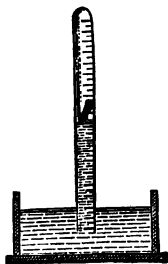
¹ Neither charcoal nor plumbago are dissolved by acid, but a mixture of nitric acid and potassium chlorate slowly attacks plumbago and gradually converts it into a solid body named *graphitic acid* by its discoverer, the late Sir Benjamin C. Brodie.

² Some varieties of charcoal made from very dense wood—boxwood, for example—and prepared at a very high temperature, conduct electricity tolerably well.

place on the non-conducting surface of the wax or other mould; hence the importance of this property of plumbago in the arts.

Experiment 225.—Fill a tube, closed at one end, and about 20 c.ms. long by 2 c.ms. diameter, with ammonia gas prepared as in Experiment 117. When full of gas, depress the open end of the tube in some mercury contained in a small basin,

FIG. 91.



as shown fig. 91, and pass up the diamond through the liquid metal and into the confined gas. Note that the volume of gas remains unchanged. Pass the specimen of plumbago into the gas in the same manner. In this case also no change of volume is noted. Now introduce, in the same way, a piece of dry wood charcoal,¹ and observe that the mercury soon begins to

rise in the tube. If the ammonia gas be quite pure and free from air, and the piece of charcoal be of sufficient size, the mercury will rise to the top of the tube, evidently owing to its complete absorption by the charcoal.

On making corresponding experiments with other gases it has been found that charcoal is an excellent absorbent of many of them, and the following table contains the results of a number of quantitative experiments on this point made by Saussure, who

¹ The charcoal acts best if made from dense wood and recently heated in an iron ladle while completely covered with sand, in order to prevent its combustion in air.

employed beech-wood charcoal, each cubic centimeter of which absorbed ¹—

Ammonia gas	90 c.cs.
Hydrochloric acid gas	85 „
Sulphur dioxide gas	65 „
Sulphuretted hydrogen gas	55 „
Nitrous oxide gas	40 „
Carbon dioxide	35 „
Oxygen	9 „
Nitrogen	6 „
Hydrogen	1 „

The dense charcoal obtained from cocoa-nut absorbs still larger proportions of these gases ; thus the late Mr. Hunter, of Belfast, found that each cubic centimeter absorbed 171 c.cs. of ammonia, 86 c.cs. of nitrous oxide, and 67 c.cs. of carbon dioxide, omitting fractions. We may here note that the gases which are absorbed in largest proportion by charcoal are also easily soluble in water.

Experiment 226.—Divide a piece of putrid meat, game, &c., in two parts ; place each in a separate beaker, and cover one piece with a layer of two or three centimeters of fresh roughly-powdered wood charcoal. Note that while the smell from the uncovered substance is strong and offensive, no unpleasant odour is perceived from that covered with the layer of charcoal. Therefore charcoal is a powerful *deodorant*. We may fairly conclude that this effect is largely due to its power of absorbing

¹ Nothing is really known as to the condition in which the gases exist within the charcoal.

gases that we have detected in the last experiment ; but it is probable that the absorbed gases or vapours also undergo slow combustion into inoffensive products by the action of oxygen necessarily present in all charcoal that is freely exposed to air.

Advantage is taken of this important property of charcoal in deodorising offensive matters ; for this purpose it is sufficient to cover the material with a layer of the fresh charcoal.

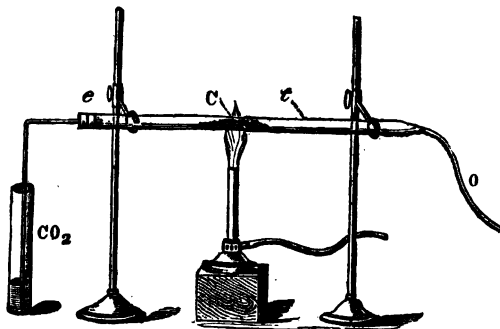
Experiment 227.—Dilute some common claret with its own volume of water, introduce it into a flask, and along with it some powdered *animal* charcoal, and boil the mixture. Then throw the contents of the flask on a filter ; a *colourless* liquid passes through, and much of the aroma of the wine has also disappeared, while the charcoal, retaining the colouring matter, remains on the filter. Wood charcoal does not possess this property in the same degree as animal black, and plumbago and diamond are wholly deficient in this absorbent power.

The decolorising power of animal charcoal is of great importance in the arts, notably in the removal of colour from syrups during the process of sugar-refining, the solutions of brown sugar being filtered through long columns of charcoal, and the colourless syrup thus obtained evaporated to the crystallising point for the production of white or loaf sugar.¹ The *animal charcoal* ordered by the British Pharmacopœia is chiefly employed for decolorising solutions of vegetable matter in the course of the preparation of the alkaloids morphia, atropia, &c.

¹ See Part IV.—Sugar.

Advantage is also taken of the absorbent power of animal and wood charcoal for bodies of organic origin by using them in the purification of water contaminated with dissolved or suspended organic matters. All the numerous forms of charcoal filters now sold are more or less effective, but it has been abundantly proved that while charcoal filters remove organic and some mineral matter from the water that passes through them, they soon cease to act save as

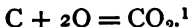
FIG. 92.



mere mechanical filters. Their special power may, however, be restored by placing the filter, dry, in an iron vessel covered with dry sand and then heating to redness, out of contact with the air. When cold, the filter may be removed from the sand, washed, and used at once for water-filtration.

Experiment 228.—Arrange the apparatus shown in fig. 92 ; *t* is a tube of hard glass, about 35 c.ms. long and rather more than 1 c.m. diameter ; it is

connected at the end *o* by means of a flexible tube with a gas-holder, bag, or flask capable of supplying a stream of oxygen. The end *e* is provided with a cork and delivery tube, as indicated, and should dip into a jar or bottle containing some clear lime-water. Introduce into the tube a few pieces of wood or animal charcoal, *c*, and apply heat to that portion of the tube on which the carbon rests, and pass a gentle stream of oxygen through the apparatus. First note that when the pure oxygen is made to bubble through the lime-water, the latter remains clear ; but soon the charcoal begins to burn in the gas, as in Experiment 58, and the issuing gas then renders the lime-water milky. We have already learned, from the experiment just referred to, that lime-water is a convenient test for the gas, which is carbon dioxide, and is always produced when carbon burns in excess of air or oxygen—



Experiment 229.—Use the same arrangement in a corresponding experiment with plumbago, and note that even when the latter is very finely powdered and heated very strongly, only a small quantity of carbon dioxide is produced ; if, however, we mix the plumbago with twice its weight of any body rich in oxygen—for example, potassium chlorate—and then heat sufficiently, combustion takes place, and much carbon dioxide is produced and detected by the lime-

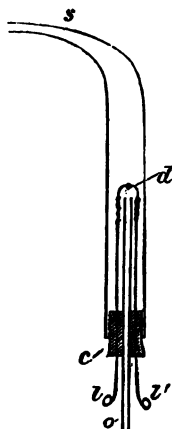
¹ It has been proved by the precise investigations of MM. Dumas and Stas that for every 12 c.grs. of carbon burned in excess of oxygen, as described, 44 c.grs. of the compound of carbon and oxygen, CO_2 , can be collected.

water. Therefore plumbago, though much more difficult of oxidation than charcoal, affords exactly the same ultimate product.

Experiment 230.—When the diamond is heated in the same apparatus as the charcoal or plumbago, it does not undergo combustion, but it can be easily burned by adopting the plan now to be described.

Bend a piece of glass tube about 1.5 c.m. in diameter, as shown fig. 93. Through the cork *c*, a glass tube should pass for conveyance of oxygen, and on each side of the tube two stout copper wires should also pass and project, as shown, beyond the internal opening of the oxygen tube. The external ends of the wires are twisted into loops, and the cork surface is well covered with wax round the tube and wires, in order that the joint may be air-tight. Connect the wires internally by means of a little spiral of rather thin platinum wire, each end of the latter being securely twisted round a clean copper wire. Before introducing the cork into the tube, slip the small diamond between a pair of loops of the platinum spiral, wherein it should be securely held at *d*, and then insert the cork in the large tube. Now let the end *s* dip under the surface of lime-water, and pass a gentle stream of oxygen through the apparatus. Next connect one of the copper loops *l* with one of

FIG. 93.



the poles of a small galvanic battery of two cells, and touch the other loop with the second battery wire. The platinum spiral offers so much resistance to the passage of the galvanic current that it speedily becomes red hot and even white hot, and the diamond held in its coil is heated to the same temperature. Care must be taken to avoid heating the platinum to whiteness, as the metal is likely to fuse and spoil the experiment ; this can be easily avoided, unless the battery is too strong, by breaking contact for a moment at a loop. When the temperature of the diamond approaches a white heat it begins to burn, and will continue to glow steadily even when the contact is broken and the wire is no longer heated by electricity, while the issuing gas renders the lime-water turbid, just as in the case of charcoal and plumbago. This combustion can be stopped by shutting off the current of oxygen ; but if it be allowed to proceed, the diamond is seen to slowly burn away almost completely, ultimately leaving a minute quantity of ash. Therefore the diamond, though difficult of combustion, can burn in oxygen, and affords the same product as charcoal and plumbago ; hence it consists of the same matter.¹

If the reader will take the trouble to tabulate the results of the foregoing comparative experiments, it will be seen that while the differences in physical characters between charcoal and plumbago are great,

¹ It has been proved by experiment that equal weights of the three forms of carbon, in pure condition, afford equal weights of carbon dioxide, and do not give any other product. 12 parts by weight of carbon in any form afford 44 parts of carbon dioxide.

the diamond is as completely distinct from the other forms of carbon as many of the recognised elements are from one another, and it only agrees with those varieties in the single particular of affording an identical product when burned in oxygen. It is not surprising, then, that the true nature of the diamond was not known until a mode of burning it was discovered in 1694 by the Florentine Academicians who effected its combustion in the focus of a concave mirror, and the identity of its product of combustion with carbon dioxide was proved by Lavoisier and by Sir Humphry Davy. In the three varieties of carbon we therefore have remarkable illustrations of the *allotropism* of an element, already referred to in the case of Ozone, page 121, Part I.

We have hitherto dealt only with well-marked and pure varieties of carbon ; but we meet with the element in many other less pure forms in the arts and in nature ; thus *lampblack* is impure and finely-divided carbon, obtained during the partial or imperfect combustion of fatty or other bodies rich in carbon ; ordinary *soot* is another impure variety, condensed from coal smoke ; *coke* is the somewhat graphitic form of impure carbon left when coal is subjected to distillation for the production of illuminating gas, or to a process of imperfect combustion in *coke ovens*. Again, *coal* is impure carbon, and is the product of the gradual degradation and consolidation of the wood of primæval forests. Woody tissue or *cellulose* is a compound of carbon, hydrogen, and oxygen whose formula is $C_6H_{10}O_5$. In process of time nearly all of the oxygen, some of the hydrogen,

and a little carbon, were eliminated in various forms of combination, and the residue, consisting of carbon with small proportions of compounds of carbon and hydrogen, retains more or less of the form of the original wood, while it has undergone the change in composition above mentioned. There is thus a gradual change of wood to *lignite*, *cannel* or highly bituminous coal, *caking coal*, and *anthracite*, the latter being nearly pure carbon. The following comparative analyses¹ of these bodies, excluding ash, enables the change of composition to be traced. 100 parts of each afforded—

	Wood (Oak, dry)	Lignite	Cannel Coal	Caking Coal	An- thracite
Carbon	50.10	66.31	80.07	86.75	90.39
Hydrogen	6.07	5.62	5.52	5.24	3.28
Oxygen (with little N and S)	43.68	25.78	11.70	6.61	4.72

Peat, or 'turf,' is the product of slow decomposition of mosses and aquatic plants; this when air-dried rarely contains less than 24 or 25 per cent. of moisture, and 6 or 8 per cent. of ash, while the proportion of carbon seldom exceeds 50 per cent. One ton of good coal can produce as much heating effect as about $2\frac{1}{2}$ tons of well-made peat of average quality.

¹ Watts's *Dictionary of Chemistry*.

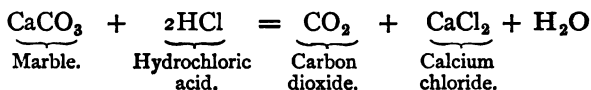
CHAPTER XX.

EXPERIMENTS WITH OXIDES OF CARBON.

CARBON DIOXIDE = CO_2 . 1 Vol of gas weighs 22 c.grs. Molecular weight = 44.—Before proceeding to prepare and experiment with coal gas it is evidently desirable to make a fuller examination than we have yet carried out of the gas resulting from the combustion of charcoal or other form of carbon in oxygen. We have already learned that the gas renders lime-water turbid, and we further know, from Experiment 88, that the same body is given off from the lungs of animals during respiration ; later on we shall find that it is evolved in the course of *fermentation* in the brewer's and distiller's vats, and during *lime-burning* in the large kilns in which limestone is commonly converted into the well-known 'quicklime' used in making mortar (see Part III. page 259).

Experiment 231.—Introduce into the bottle used in the preparation of hydrogen, fig. 8, some lumps of broken limestone, or, better still, the purest form of the same compound—white marble, and cover the latter with some water. Now pour in through the thistle funnel some strong hydrochloric acid ; almost immediately effervescence begins, and a colourless and nearly inodorous gas escapes ; if this be passed through the delivery tube into some lime-water, a

white cloud or precipitate of chalk will form, indicating, as far as this test goes, that the same gas is produced in this case as in the others already cited. The following equation expresses the change consequent upon the action of the acid on the chalk—



Experiment 232.—Collect a jar of the gas over water in the usual way, remove it with a glass plate, and place it mouth upwards. Slip away the plate and plunge into the gas a burning taper. It is instantly extinguished. Therefore carbon dioxide is not only a colourless, almost inodorous gas, incombustible in air, but it does not support the combustion of a taper.

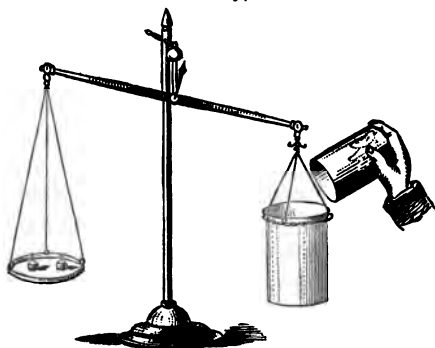
Experiment 233.—Fill another jar as before, and remove from the trough. Take a second jar, dry, and containing only air; place it mouth upwards. Test the contents of the latter with the taper, which should, of course, burn freely in the jar; remove the taper, and then slowly pour in the carbon dioxide gas from the first jar. Again test the contents of the jar that previously contained air, and it will be found that the taper is extinguished. Therefore carbon dioxide is sufficiently heavy to pour from one vessel to another like a liquid, though no matter is *seen* to pass.

The specific gravity of the gas is 22 ($H = 1$); hence its molecular weight is 44, and its formula CO_2 (if $C = 12$). Carbon dioxide is therefore about one and a half times as heavy as air. It is evident, then, that

we might collect it by downward displacement of air instead of over water.

Experiment 234.—Allow the delivery tube of the gas bottle to dip into a large jar whose mouth is partially closed by a piece of cardboard, and pass a stream of carbon dioxide into the vessel, of course maintaining the evolution of gas by occasional addition of fresh acid through the funnel tube. While this filling is in progress, attach a large beaker by

FIG. 94.



slings of copper wire to the arm of a rough scales, as shown in fig. 94, and counterpoise. Now ascertain by means of the burning taper whether the jar is yet full of gas ; if so, bring the jar near to the counterpoised beaker and pour the gas into the beaker without touching the latter. As the beaker fills with the heavy carbon dioxide gas it overbalances the weight in the opposite pan, thus proving, in a very interesting and complete way, that the gas is heavier bulk for bulk than ordinary air.

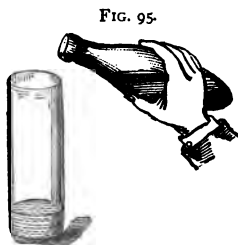
By a method analogous in principle to that employed in the liquefaction of ammonia gas in Experiment 119 (i.e., by mechanical compression), carbon dioxide can be obtained as a colourless liquid.¹ When the liquefied carbon dioxide is allowed to issue into the air in a thin stream it evaporates so rapidly that the heat abstracted is sufficient to freeze the residue, which latter appears as a white solid body resembling snow. A mixture of this 'snow' with ether is the most powerful freezing mixture known, and with it mercury can be easily solidified. The pressure required for the liquefaction of the gas is so great—about 50 atmospheres at the mean temperature—that very strong and costly apparatus is required for the purpose; and since the condensation is attended with some danger, it is not advisable for the junior student to attempt experiments in this direction.

Experiment 235.—Fill a jar with the gas, then introduce some water; close the mouth of the jar with the palm of the hand, and shake vigorously. Note that the hand is held by suction to the mouth of the jar, indicating that the gas has been absorbed by the water. Note that the water acquires a brisk taste, and a slight *acid* reaction to litmus-paper. 1 cubic centimeter of water dissolves 1.002 cubic centimeters of the gas at 15° C.

Experiment 236.—Obtain a bottle of 'soda water,'

¹ The specific gravity of this liquid at - 10° C. is 0.995, but at + 20° C. it is only 0.826; it therefore expands *more than the gas* for an equal rise of temperature, since its specific gravity at + 20 would be 0.893 if it expanded at only the *same* rate as a gas.

and have ready a jar or wide-mouthed bottle containing lime-water. Now open the bottle of aerated water, and, after the first rush of gas, but while effervescence continues, bring the mouth of the bottle and of that containing the lime-water together, as shown fig. 95, and keep in this position for a short time ; then shake the lime-water with the gas in the jar, and note that turbidity is instantly produced. Therefore the gas that escapes from 'soda water' is carbon dioxide. In fact, the liquid sold is little more than a solution of the gas in water, obtained¹ and retained under moderate pressure ; for, though the *volume* of gas dissolved is the same for all pressures, the *weight* is directly proportional to the pressure ; hence on relaxing the latter the gas expands and the excess escapes.²



By the same method it can be easily proved that other aerated drinks, including champagne and other 'sparkling' wines, owe their briskness to dissolved carbon dioxide, and the same gas can be collected during the frothing of beer, porter, &c.

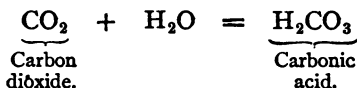
¹ The gas is generated by the action of sulphuric acid on chalk and washed by passing through water ; it then enters a pump, whence it is forced into cylinders containing water ; the latter is then charged with the gas under pressure, and is drawn off into the well-known stout bottles, into which a small quantity of solution of 'bicarbonate of soda' is poured before the aerated water is filled in.

² See Henry's (often termed Dalton's) law, Part I., p. 132.

Experiment 237.—Saturate about a liter of water with carbon dioxide gas under the atmospheric pressure by passing a slow current of the gas through distilled water for half an hour or so, occasionally shaking the gas and water together so as to facilitate absorption. In this case it is advisable to wash the gas issuing from the apparatus by making it bubble through a little water contained in a wash-bottle, so as to remove any hydrochloric acid that might be mechanically carried over by the current of gas. On testing the pure solution of carbon dioxide in water it has a distinctly *acid* reaction to blue litmus-paper. Now add clear lime-water gradually, and test with both blue and red litmus-paper after each addition. Note that a precipitate is soon produced, and *the acidity disappears*, and if the addition of lime-water be continued the liquid becomes alkaline. Here, then, the alkaline lime-water has neutralised the acid liquid. Now allow the turbid mixture to stand until the white chalk has deposited completely ; then pour away the clear liquid, and add to the white deposit a few drops of hydrochloric acid, when the precipitate dissolves with brisk effervescence, and the gas evolved can be proved as before to be carbon dioxide.

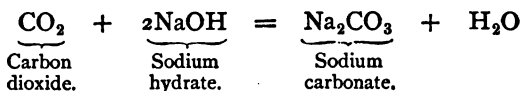
The precipitated chalk obtained by neutralising the acid liquid is found on analysis to have the composition indicated by the formula CaCO_3 . It is therefore the neutral calcium salt of a particular acid whose formula must be H_2CO_3 , for we know that Ca is a diad metal, and its atom cannot displace less than two atoms of monad H from an acid. The obvious inference is that the solution of carbon dioxide

gas contains the free acid resulting from the union of the dioxide with the elements of water, thus—



Hence CO_2 is to be regarded as an acid anhydride, and all similar experiments confirm this conclusion ; but the free acid has not yet been isolated, and is only known in its very dilute aqueous solution, prepared as above. So easily is this solution decomposed that a very gentle heat suffices to drive off the anhydride and leave a liquid which will not give any precipitate with lime-water.

Experiment 238.—Fill a tube with carbon dioxide and quickly pour in a few cubic centimeters of caustic soda solution ; close the mouth of the tube with the thumb and invert over mercury. Note that absorption soon begins, and the gas, if pure, is completely absorbed by the caustic alkali—



The carbonate thus produced can be crystallised out from the solution in the tube.

Experiment 239.—Pass a current of carbon dioxide gas through lime-water. The usual precipitate of calcium carbonate or ‘chalk’ is formed ; but note that on continuing the current of gas the liquid becomes less turbid, and ultimately *quite clear*. The chalk therefore dissolves in excess of carbonic acid water.

Experiment 240.—Take a portion of the solution obtained in the last experiment, and—

a. Expose some to the air in any shallow glass vessel. Note that a semi-transparent, somewhat crystalline, crust forms on the surface after some hours. This crust, when collected and examined, proves to be the chalk or calcium carbonate deposited again from solution. The free exposure of the liquid to the air evidently permits the escape of the carbon dioxide from the water, and the consequent loss of the body required to retain the chalk in solution.

b. Place some of the liquid in a bottle, and add to it, drop by drop and with occasional shaking, a solution of white soap in water. Note that the liquid becomes turbid, but does not produce a persistent froth or 'lather' at first; and a considerable proportion of soap solution must be added before the lather is produced. Water that thus uses up without effect, or destroys, much soap before a lathering or detergent solution is obtained, is said to be 'hard'; and the degree of hardness is determined by measuring the amount of soap it can destroy.

c. Boil some more of the solution in a test-tube or flask. Note that the liquid becomes turbid, a precipitate of chalk separating as in the last case, and in part attaching itself to the sides of the vessel. By continued boiling, almost every trace of the calcium or lime salt can be separated from solution. Pour off some of the clear liquid, and shake with a little soap solution. Note that a very little of the latter suffices to cause a 'lather'; therefore boiling 'softens' the water.

d. Add to another quantity lime-water until the liquid, when well mixed, causes a faint blue colouration of *red* litmus-paper, and therefore is *faintly* alkaline. Note that a considerable white precipitate is formed. Now filter the mixture and boil some of the colourless liquid that passes through the paper ; no turbidity should result, proving the absence of dissolved chalk ; while a few drops of acid poured over the white matter on the filter will cause much effervescence. Therefore, by the addition of lime-water to the solution of chalk in carbonic acid, the chalk is precipitated, and *along with it the lime added*. A little consideration explains the apparent paradox, for the lime-water evidently must combine with the free carbonic acid and form the chalk which precipitates, but along with the latter must fall the chalk originally held in solution by the free carbonic acid. If the proportion of lime-water added be just sufficient to combine with all the free carbonic acid, the filtered liquid should be wholly free from lime salts. Moreover, when tested as before with soap solution, it should afford a lather with a very small proportion of soap ; therefore the lime-water treatment *softens* the water when properly carried out.

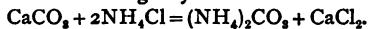
The foregoing experiments throw a great deal of light on some phenomena of general interest. Thus, the *stalactites* observed in limestone and other caverns consist for the most part of calcium carbonate in more or less crystalline condition ; these are formed by the gradual deposition of calcium carbonate from water trickling through fissures in the roof, the solvent carbon dioxide escaping on exposure to the

air. The drip from the growing stalactite deposits on the floor a further quantity of its chalk, and thus a conical mound, called a *stalagmite*, rises to meet the depending stalactite.

Again, the *furring* of domestic kettles and boilers is due primarily to the deposition of impure chalk from the boiling water, as a more or less adherent layer on the inner surfaces. When the layer becomes thick it seriously interferes with the transmission of heat, as the deposited matter is a bad conductor of heat; hence the coating must be occasionally scraped off. In the cases of steam boilers, much loss and inconvenience often arise from this cause.

Various plans have been adopted for either preventing the deposition of chalk,¹ or, better still, for removing it from the water prior to use. In the latter case lime-water is added in sufficient quantity to precipitate all the free carbonic acid and the chalk previously in solution. The turbid mixture is allowed to stand in large tanks, in order that the whitish chalk may deposit, and the clear and softened water is then drawn off for use. In dealing with water on a large scale, it is necessary to determine its degree of '*temporary hardness*'—i.e., the hardness removable by boiling.² Then in the treatment of 100,000 gallons in a large tank, we use seven pounds of lime for

¹ Sal ammoniac is often used for this purpose, since it acts upon chalk in the following way:—



The ammonium carbonate volatilises with the steam, and the very soluble calcium chloride remains in the boiler.

² For the method of estimating this, and full explanation of the reaction, see Part IV. under SOAP.

every degree of temporary hardness of the water. The lime must first be slaked and stirred with some of the water to a thin cream ; when added to and thoroughly mixed with the bulk, subsidence of the deposit may be allowed, and in due time the softened water can be drawn off. The *rationale* of this operation has been already explained in the course of Experiment 140, *d*.

This mode of softening water is due to the late Dr. Clark, of Aberdeen, and is often spoken of as Clark's process. It is only capable of softening water that is '*temporarily hard*.' If the water contains calcium sulphate or chloride, these salts likewise cause 'hardness' and destroy soap ; but the hardness due to the presence of these salts (or to analogous compounds of magnesium) is not removable by boiling, and is said to be *permanent hardness* ; for the compounds named, unlike chalk, are independently soluble to a considerable extent in pure water, and therefore are not deposited from the latter by mere boiling or by moderate evaporation.

We have already seen (Experiment 232) that a taper does not continue to burn in an atmosphere of carbon dioxide, neither does the process of animal respiration proceed in such an atmosphere, and death is very rapid. The same result follows the respiration of an atmosphere containing 20 per cent. of carbon dioxide,¹ though the effect is not produced so quickly ;

¹ In the pure gas, spasm of the glottis is the immediate cause of death, but when diluted it seems to act not only by excluding oxygen, but also by preventing the usual exhalation of carbon dioxide from the blood, and thus stopping the purifica-

and even when the proportion does not exceed 10 per cent., insensibility is soon produced, and death follows unless an abundant supply of pure air or oxygen is quickly obtained. It is obviously undesirable for the student to undertake experiments on this point.

Experiment 241.—Place a jar full of air mouth downwards in the water of the pneumatic trough, then allow about one-tenth of its volume to escape, and replace by carbon dioxide from the apparatus already used. Having closed the mouth of the jar with a glass plate, remove and invert the jar again; change its position several times, so as to mix the gases, then place it mouth upwards and plunge into the mixture a taper or candle which is burning steadily. Note that while the candle continues to burn the character of the flame alters, its luminosity is diminished, and it is very soon extinguished, unless the jar happens to be a wide one. If the proportion of carbon dioxide much exceeds 10 per cent. the candle flame is extinguished, but if the proportion be less than 10 per cent. the effect on the flame is but slight. Therefore, while an atmosphere in which a candle cannot burn will be certainly fatal to a man, that in which a candle burns easily may be dangerous, for air that contains but 1 or 2 per cent. of carbon dioxide gives rise to a sense of oppression, soon followed by depression, headache, and vertigo. As

tion constantly in progress and essential to the continuance of life; for an artificial atmosphere containing the normal proportions of oxygen, but having a part of its nitrogen replaced by carbon dioxide, has been found to destroy animal life.

already stated (see p. 20), air that contains more than '06 per cent. is to be regarded as impure and unwholesome, and all efforts at ventilation must aim at maintaining a higher degree of purity. It therefore becomes a matter of practical importance to determine whether a given sample of air is or is not of the required degree of purity. Thanks to the patient labours of Dr. Angus Smith, of Manchester, we are now acquainted with a very simple method for the determination of this point, and further for the recognition of the dangerously impure air that the candle test fails to detect. This is specially important, since carbon dioxide, owing to its high density, tends to collect in low-lying places near to any source of the gas; for example, in the neighbourhood of limekilns, in caverns, wells, mines (and carbon dioxide is the chief constituent of the 'after-damp' or 'choke-damp' found in a coal mine after an explosion of 'fire-damp'¹), in cellars, in the holds of ships, and in the fermenting vats of brewers and distillers.

Dr. Angus Smith's process depends upon the fact that clear saturated lime-water can dissolve about $\frac{1}{84}$ th of its volume of carbon dioxide at ordinary temperatures without becoming turbid, because sufficient water is present to hold in solution the minute quantity of chalk or calcium carbonate formed, since the compound is not quite insoluble in pure water. If, however, the proportion of carbon dioxide dissolved exceeds that above stated, the liquid becomes turbid as the excess of chalk separates. It is, therefore, evident that the easily obtained lime-water becomes

¹ See p. 180.

a convenient test of the condition of a given sample of air, if we know the maximum volume, containing 0.06 per cent. of carbon dioxide, that can be shaken up with lime-water without causing turbidity. Dr. Angus Smith found that one volume of the solution could be shaken up with twenty volumes of air containing 0.06 per cent. of carbon dioxide without the production of any turbidity, but that a very slight increase in the proportion of carbon dioxide led to the production of a precipitate. The most convenient and practical mode of applying the test is the following :—

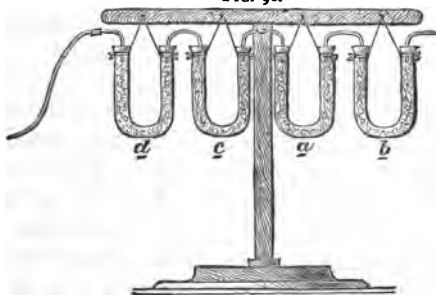
Experiment 242.—Select a well-stoppered bottle of clear white glass, capable of containing, when quite full, ten and a half fluid ounces of water as nearly as possible. Take care that the bottle is perfectly clean and dry. Now fill the bottle with the air to be tested by sucking out that in the bottle through a long glass or flexible tube ; great care must be taken to prevent any expired air passing into the vessel, or air from the immediate neighbourhood of a candle or gas-burner. Next introduce half a fluid ounce of clear lime-water, insert the stopper, and shake vigorously for ten or fifteen seconds ; let the bottle stand, in order that air-bubbles may rise, and note whether or not turbidity or opalescence is produced. If the liquid does not remain bright and clear the air examined contains more than 0.06 per cent. of CO_2 ; but if no turbidity is produced the sample tested is wholesome, *ceteris paribus*.

When more precise determinations are required we have recourse to the following method, which

combines the estimation of moisture with that of carbon dioxide in the air.

Experiment 243.—Fill with water the aspirator employed in Experiment 26, and connect it by means of the flexible tube with apparatus shown in fig. 96. The light U-tubes *a* and *b* contain pumice-stone moistened with strong and pure oil of vitriol, while *c* contains fragments of solid caustic potash moistened with a little water, and *d* is another pumice and sul-

FIG. 96.



phuric acid tube ; all are connected by flexible tubes, and *d* with the aspirator. *a* and *b*¹ are weighed together before an experiment, and the weight of *c* and *d* also ascertained ; the connections are then made, and water allowed to drop from the aspirator into a vessel of known capacity in liters placed to receive it. As the air passes through the apparatus it parts with its moisture in *a* and *b*, and with its carbon dioxide²

¹ These two tubes need not be weighed if an estimation of the moisture in the air be not desired, but they cannot be omitted from the arrangement.

² The carbon dioxide forms potassium carbonate. (See Experiment 238, an analogous action of caustic soda.)

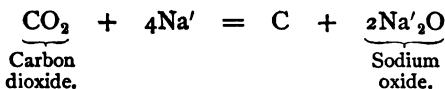
in *c*, while any moisture derived from *c* is retained in *d*. Therefore, in weighing after the experiment, the gain in weight of *a* and *b* gives the *moisture* in the volume of air drawn through the apparatus, and the gain of *c* and *d* the carbon dioxide in the same volume. It is desirable to draw about 50 liters of air through the tubes ; if the aspirator used be small there is no objection to refilling at necessary intervals, but the total volume of water that runs from the aspirator must be accurately known, as it is the measure of the volume of air. It is necessary to note the temperature and pressure at the time of the experiment.

The weight of carbon dioxide found must then be calculated into the volume of the gas at the temperature and pressure of the experiment, as explained in Chapter X., and the proportion in the air thus directly determined. Thus, 50 liters of air at 10° C. and 760 m.ms. pressure afforded 3.7 c.grs. of CO₂.

Now 1 vol, or 112 c.cs. of CO₂ weighs 22 c.grs. ; consequently 3.7 c.grs. measure 18.8 c.cs. at 0° C. and 760 m.ms., and 19.48 c.cs. at 10° C. (see Part I., page 101). This is the volume of CO₂ in 50 liters (= 50,000 c.cs.) of air, or 0.0389 per cent.

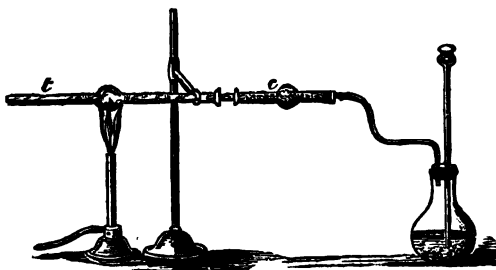
Experiment 244.—Place in the bulb of the tube *t*, fig. 97, a few pellets of clean metallic sodium, and pass over the latter a current of carbon dioxide from the bottle, as shown, interposing between the latter and the tube the drying tube *c* filled with fragments of calcium chloride. When *t* is full of gas, apply gentle heat to the sodium in the bulb, and note that the metal soon melts and then begins to act upon the gas, quickly separating black *carbon* from it, thus affording

proof of the presence of the element in the gas. Glowing accompanies this change, hence sodium evidently burns in the gas, owing to its high attraction for oxygen, and sodium oxide results—



Experiment 245.—We are now encouraged to try another metal that we already know to possess a great attraction for oxygen—namely magnesium. Fill a jar

FIG. 97.



with carbon dioxide gas and plunge into it a wire of magnesium while freely burning in air. Note that the metal continues to burn in the gas if the combustion in air be vigorous at the outset; in other words, if the metal be raised to a sufficiently high temperature to decompose the gas.

CARBON MONOXIDE = CO. 1 Vol weighs 14 c.grs.
Molecular weight = 28.

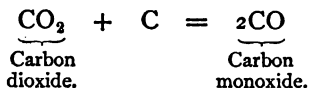
Experiment 246.—Plunge a piece of incandescent charcoal into another jar of gas. Note that the com-

bustion of the charcoal ceases. It may be, however, that the temperature to which the charcoal has been raised is not sufficient to partially decompose the gas, for it is evident that we could not look for *complete* deoxidation of carbon dioxide by charcoal ; hence we shall modify the experiment as follows :—

Experiment 247.—Fill the gun-barrel used in Experiment 48 with small pieces of charcoal, and pass it through the table furnace employed in that experiment. Now close each end by a well-fitting cork, and through each cork pass a piece of glass tube. While the gun-barrel and its contents are heating, connect one end with an apparatus affording a stream of carbon dioxide, and pass the current for some time, so as to fill the tube with the gas. Having previously obtained two bladders, of equal capacity, and softened them by immersion in water, or two small elastic bags of one or two liters capacity, fit each with a piece of glass tube of the same diameter as that which passes through the corks of the gun-barrel. Now fill one of the bags with carbon dioxide and attach it by means of a flexible tube to the end of the gun-barrel opposite to the evolution flask, then remove the latter and quickly connect in its place the second bag, previously emptied of all air or gas. By compressing the bag full of gas the latter can be made to pass *slowly* over the red-hot charcoal into the bag previously empty, and the gas thus passed and repassed from bag to bag. If the temperature of the charcoal in the tube be that of full redness, the volume of gas will steadily increase until *both* bags become full of gas, and the original volume has therefore been doubled.

This effect is, of course, in part due to the increase of temperature of the mass of gas, but if the receiving bag used in the first instance be much larger than that from which the gas is first forced over the charcoal, and the action of the charcoal on the carbon dioxide be complete, and further, if the gas be allowed to cool down to the initial temperature, the resulting volume of gas is found to be really double that of the carbon dioxide used.

Now remove one of the bags, slightly compress it so as to make the contained gas issue from the glass tube as a colourless jet, and apply a flame. The issuing gas *burns* with a fine blue flame. This combustible gas is found on examination to be a lower oxide of carbon than that previously experimented with, and its composition is indicated by the symbol CO. This gas is evidently the result of the *partial* combustion of carbon in its highest oxide, thus—



Therefore one molecule of carbon dioxide in taking up another atom of carbon splits up into two molecules of the monoxide—hence the doubling of volume detected.

A precisely similar deoxidation of carbon dioxide by carbon is of frequent occurrence in ordinary fire-places and furnaces. The air entering between the fire-bars meets with red-hot coal and produces therewith carbon dioxide gas ; the latter, accompanied by the nitrogen of the air, passes up through the burning

mass and then partial deoxidation of the carbon dioxide occurs, since red-hot carbon is present in great excess ; the resulting carbon monoxide may then be seen to burn with its usual blue flame above the coals, where it meets with fresh air. In furnaces, where little air enters above the fuel, the heated carbon monoxide is carried up the chimney and burns at the top, and at night its blue flame may often be seen arising from factory stacks. The gas is also produced in all cases of combustion of carbon or carbonised materials in an insufficient supply of air ; thus, charcoal burning in the centre of a badly ventilated room, in a wire cage, or chauffer, develops much carbon monoxide, and the atmosphere quickly becomes impure.

Air containing less than 1 per cent. of carbon monoxide is poisonous to man and other animals, and, owing to the ease with which the poison is produced, suicide by means of charcoal fumes is very common, especially in France. In these cases death is due to the direct action of the monoxide. The primary effect of the gas is prostration of strength, followed by drowsiness, then complete insensibility, and death. In the early stages of the poisoning the effects may be counteracted by removal of the person into fresh air and the promotion of free respiration ; in extreme cases it is necessary to oblige him to inhale pure oxygen for some time. Recovery from carbon monoxide poisoning is much more difficult than from that caused by the dioxide, because the former body, unlike the dioxide, is now known to unite directly with the red colouring matter of the blood—hæmoglobin—and form with it a tolerably stable compound,

from which the oxide of carbon is but slowly displaced even by pure oxygen. Now this hæmoglobin is the constituent of the blood that acts as the carrier of oxygen from the lungs throughout the body, and it thus acts by forming a feeble compound with the oxygen of the air ; if, however, carbon monoxide be united with the hæmoglobin instead of oxygen, the vital processes involving oxidation no longer take place, and death soon ensues.

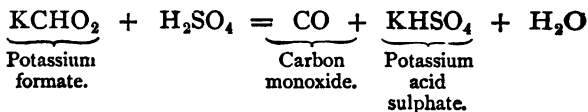
If in the last experiment we pass a current of steam instead of carbon dioxide over the red-hot carbon, a mixture of carbon monoxide and hydrogen is obtained, thus—



This reaction has often been applied on the large scale in the production of a cheap gas suitable for heating purposes, though not for use as an illuminating material ; but it would be obviously imprudent to introduce so poisonous a mixture into our houses.

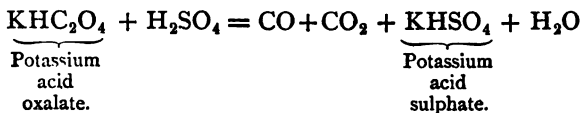
Experiment 248.—Heat a small quantity of potassium formate— KCHO_2 —with a little strong sulphuric acid in a test-tube. Note that gas is evolved with effervescence, and that on bringing a flame to the mouth of the tube the gas takes fire and burns with a blue flame, like the carbon monoxide prepared in the last experiment.¹ In this case—

¹ Another process that may be employed for the production of the gas consists in heating a mixture of strong sulphuric acid with potassium ferrocyanide. For this method see 'Cyanogen Compounds,' p. 201.



A glass rod moistened with lime-water, and introduced into the tube *before* the gas is burned, is not coated with chalk.

Make a similar experiment to the last with some crystals of acid potassium oxalate— KHC_2O_4 —instead of the formate, and note that much gas is evolved on heating, and that it can be made to burn with a blue flame as before. It is probable, therefore, that carbon monoxide is evolved in this case likewise, and its production from the oxalate admits of easy explanation by the following equation, if we assume that carbon dioxide is separated at the same time:—

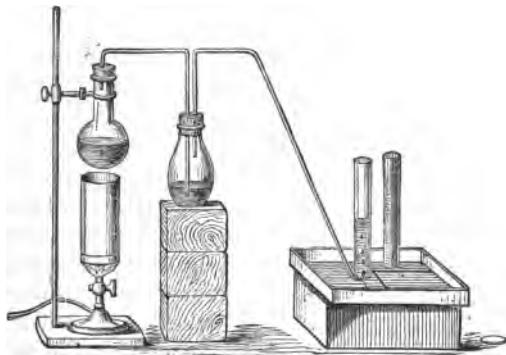


The presence of CO_2 in the gas can be easily proved by holding in the *unburned* gas a rod moistened with lime-water; the latter is quickly rendered milky. If, then, we could dissolve out the carbon dioxide from the gas, pure carbon monoxide should be easily obtained from the oxalate, or, more economically still, from free oxalic acid. The comparative tests with lime-water indicate a mode of effecting the desired separation.

Experiment 249.—Arrange a flask as shown

(fig. 98), and connect it with the wash-bottle, while from the latter proceeds the gas delivery tube. Introduce into the flask 10 or 12 grams of crystallised oxalic acid, and about 60 c.cs. of oil of vitriol. Half fill the wash-bottle with 'milk of lime.'¹ Now cautiously apply heat to the flask, and when effervescence begins regulate the temperature so as to maintain a

FIG. 98.



slow but steady current of gas through the milk of lime. After the expulsion of ordinary air from the apparatus, gas passes unabsorbed through the wash-bottle, and can be collected in jars over the water in the trough. A jar full of gas when removed, and a flame applied to its mouth, burns with a blue flame. Hence, carbon monoxide is not absorbed by the lime,

¹ Obtained by 'slaking' with water some quicklime, and stirring the product with water until a thin cream is formed; the latter is then poured off into the wash-bottle. Strong solutions of caustic soda or potash serve the same purpose.

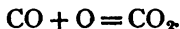
though we know that most of the carbon dioxide must be separated in this wash-bottle. Collect several jars of the gas, let them stand over water for some hours in order to remove the remaining carbon dioxide, and then note—

a. That it is a colourless gas with a scarcely perceptible odour, and is very slightly soluble in water; 1.00 c.c. dissolves only 0.024 c.c. at 15° C.

b. That it is combustible, but does not support the combustion of a taper.

c. That it is not heavier, but rather lighter, than air; and therefore cannot be poured out like the dioxide. One *vol* weighs 14 c.grs.;¹ consequently, its molecular weight is 28, and its formula CO.

d. That lime-water, when added to a jar of the *well washed gas*, does not become turbid, or that the turbidity produced is slight;² but that the same gas when burned—the mouth of the tube being quickly closed by a glass plate—and its product of combustion shaken with the lime-water, causes strong milkiness; therefore, CO₂ is its product of combustion in air—



Consequently, if two volumes (representing the molecule) of the monoxide are mixed with one volume (a semi-molecule or atom) of oxygen, two volumes (or one molecule) of carbon dioxide should result.

¹ One *vol* of air weighs 14.47 centigrams.

² It is very difficult to remove the last traces of carbon dioxide, except by long standing in contact with milk of lime or caustic soda.

Experiment 250.—Fill a jar standing over water two-thirds with carbon monoxide and the remaining third with oxygen, and apply a flame to the mixture. A flash and sharp report follow. If the experiment be made in the eudiometer over mercury, a condensation of one-third takes place after explosion, and the residual gas is completely absorbed by caustic soda or potash.¹

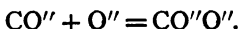
Experiment 251.—Fill a tube with carbon monoxide gas over mercury, and pass up into it, by means of a curved pipette, some solution of cuprous chloride— Cu_2Cl_2 .² Note, that, on standing, the gas is completely absorbed, and, if pure, ultimately disappears; but when the tube is removed from the mercury, after closing its mouth with a thumb, then inverted, and the solution poured into a test-tube and heated, the gas is expelled from the liquid. Advantage is sometimes taken of this property of carbon monoxide in the determination of its proportion in gaseous mixtures.

All the facts observed lead to the conclusion that carbon monoxide is a much more active body chemically than the dioxide, which is the highest known oxide of carbon. We therefore conclude that the

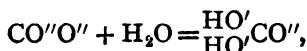
¹ The attraction of CO for one atom of oxygen at high temperatures enables us to employ it as a powerful reducing agent for metallic oxides, and it may be substituted for hydrogen in Experiment 52. Carbon monoxide is the chief agent in reducing zinc from its oxidised ores, *q.v.*

² Prepared by dissolving black oxide of copper to saturation in hydrochloric acid diluted with three times its volume of water, and then digesting the solution in a stoppered bottle with copper turnings until the liquid becomes colourless.

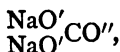
links or bonds of the carbon atom in the former are not fully satisfied by those of a single oxygen atom, while in the dioxide the satisfaction with oxygen seems to be complete. Now, the oxygen atom is diad, and the inference is fairly drawn that the carbon atom is *tetrad* since it is satisfied by two oxygen atoms, and is not known to combine directly with more than two, save in union with other elements. The *group* CO ought, therefore, to act as a diad compound radicle, and it seems so to act in combining with oxygen¹ to form the dioxide; a reaction which, on this view, may be written—



Thus, carbon dioxide may be viewed as the oxide of *carbonyl*, as the group CO'' has been termed, and carbonic acid—H₂CO₃—as carbonyl hydrate, thus:—



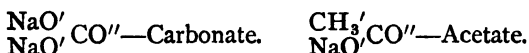
the two monad hydroxyl groups (see Part I. page 141) satisfying the diad carbonyl, the latter thus appears to be the *radicle of carbonic acid*, and therefore of *all carbonates*. Thus written, the formula of sodium carbonate is—



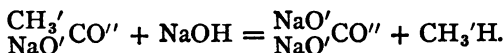
the monad group NaO' replacing hydroxyl in the acid.

¹ CO also unites with its own volume of chlorine under the influence of sunlight, and forms the gas COCl₂, originally termed *phosgene* gas, or carbonyl chloride.

Experiment 252.—Place a few grams of common crystallised sodium carbonate in an evaporating dish with some water, heat nearly to boiling, and add acetic acid, or vinegar, until effervescence ceases; then evaporate the solution to dryness. The residue consists of *sodium acetate*, whose empirical formula is $\text{NaC}_2\text{H}_3\text{O}_2$. It is evidently possible to write this formula in such a way as to trace a relationship between the sodium acetate and carbonate, thus—



In the former both bonds of CO'' are satisfied by monad NaO' groups; in the acetate but one bond is so satisfied, while the second is engaged with another group, CH_3 , which must also be a monad if the carbon atom be tetrad. If this view be correct, it ought to be possible to replace the CH_3' radicle by NaO' , on treatment with caustic soda, thus—



And such a reaction should afford us the tetra-hydride of carbon. In the next chapter we shall put this induction to the test of experiment.

CHAPTER XXI.

EXPERIMENTS WITH HYDROCARBIDES, COAL GAS, ETC.

MARSH GAS, CARBON TETRAHYDRIDE (or *Methane*)
 $=\text{CH}_4$. 1 Vol weighs 8 c.grs. Molecular weight
 $= 16$.

Experiment 253.—Mix in a mortar a gram or two of the dry sodium acetate with half its weight of dry caustic soda rapidly powdered ; introduce the mixture into a test-tube, and heat. Presently colourless gas is evolved, which can be ignited at the mouth of the tube, and there burns with a slightly luminous flame, quite unlike that of carbon monoxide, though, like the latter, it produces abundance of carbon dioxide during combustion. We shall next prepare a quantity of the gas, and examine it.

Experiment 254.—Introduce a larger amount of the mixture used in the last experiment into a flask fitted up as described for the preparation of oxygen ; heat and collect the evolved gas over water in jars as usual, but take care to remove the delivery tube from the water before gas ceases to be evolved ; dry the end of the tube and connect it with a chloride of calcium tube similar to that used in Experiment 20. Continue to heat the contents of the flask, and then

ignite the gas issuing from the drying tube, and note that a cold body held in the flame becomes bedewed with moisture. Therefore *hydrogen* is a constituent of the gas.

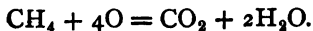
a. Shake up some of the gas with lime-water ; note that no turbidity is produced.

b. Remove a jar in the usual way, holding it mouth downward, and apply a flame ; the gas burns with a more luminous flame than hydrogen. When the combustion is nearly over, close the mouth of the jar with a glass plate ; invert, and pour in a little lime-water by slipping aside the plate for an instant. When the products of combustion are shaken up with the lime-water, the latter becomes turbid, proving the production of carbon dioxide on combustion.

c. Prove that the gas is lighter than air as in the experiment with hydrogen (19, *b*). The specific gravity of the gas is 8^1 ($H=1$), and 1 vol weighs 8 centigrams ; therefore the molecular weight of the gas is 16, and this accords with the formula CH_4 if the atomic weight of carbon be taken as = 12.

d. Shake up some of the gas with water ; very slight absorption takes place. 1 c.c. of water dissolves only 0.039 c.c. of the gas at $15^\circ C$.

e. Mix in a small stout tube one volume of marsh gas with twice its volume of oxygen ; remove from the trough, and apply a flame to the mixture ; a violent explosion occurs, and carbon dioxide and water result, thus—



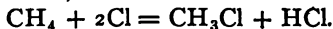
If air be used instead of pure oxygen the mixture

¹ Sp. gr. of air = 14.47, if $H=1$.

explodes, and affords the same products, but marsh gas requires ten times its volume of air for complete combustion.

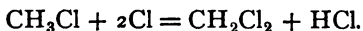
The body whose chief properties we have now noted is commonly termed *marsh gas* because it is met with in the bubbles of gas that rise on stirring marshy pools in which decomposing vegetable matter occurs. The same gas often issues in abundance from rifts in coal seams, and is termed *fire-damp* by miners. When mixed with air and the mixture ignited by a flame,¹ it causes the violent explosions in coal mines which annually result in great loss of life. The explosion of fire-damp mixture in a mine causes death by direct shock ; but those who escape or may enter a mine after an explosion are often killed by the products of combustion—*after-damp* or *choke-damp*—the principal of these being carbon dioxide.

Experiment 255.—Mix marsh gas with its own volume of chlorine gas in a stoppered bottle and expose the mixture to sunlight. No rapid change takes place, but the colour of the chlorine disappears, and the jar when opened is found to contain hydrochloric acid, which reddens blue litmus-paper, and a new gas whose composition is represented by the formula CH_3Cl . This body is evidently the result of the *substitution* of an atom of chlorine for one of hydrogen in marsh gas, the displaced hydrogen uniting with another chlorine atom and forming therewith hydrochloric acid, thus—

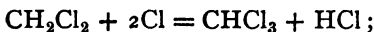


¹ See page 192 for description of the Davy safety-lamp for coal mines.

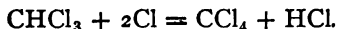
By the continued action of chlorine on marsh gas further substitution takes place, thus—



And when the third stage of this substitution is reached we get *chloroform*, CHCl_3 , our well-known anæsthetic, as the product, thus—



while by the action of chlorine on chloroform the last atom of hydrogen can be eliminated and carbon tetrachloride obtained, thus—



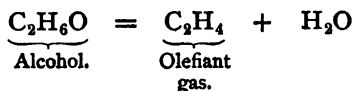
This kind of change is very common in the chemistry of carbon compounds—that great department of the science which has been termed ‘Organic Chemistry,’ and we must refer to Part IV. for additional examples, as well as for other derivatives of marsh gas; but we may point out that the above series of reactions prove marsh gas to be a *saturated* compound, for chlorine enters the molecule only by displacement of hydrogen, and not by addition to CH_4 ; thus we have further evidence that carbon is a tetrad or four-link element.

OLEFIANT GAS (*Heavy Carburetted Hydrogen, Ethene, or Ethylene*) = C_2H_4 . 1 Vol weighs 14 c.grs. Molecular weight = 28.—In the course of Experiment 247 we learned that a molecule of carbon dioxide, when heated with carbon, takes up the latter and affords two molecules of the lower oxide CO. Analogy would lead us to expect that marsh gas.

when similarly treated with carbon, would afford a lower hydride, represented by the formula CH_2 . No such change has however been realised, nor are we acquainted with any hydrocarbon whose molecule can be represented by such a formula ; but the polymeric body C_2H_4 exists, and can be easily obtained by the indirect method of abstracting the elements of water from common alcohol ($\text{C}_2\text{H}_6\text{O}$).

Experiment 256.—Introduce into a flask about 100 c.cs. of strong oil of vitriol, and add to it slowly and with frequent agitation 50 c.cs. of ‘spirit of wine.’ Insert the cork, which should be provided with a gas delivery tube similar to that used in the preparation of oxygen ; arrange the flask in a retort stand, and gently heat. Gas is soon evolved, and can be collected as usual over water after air has been expelled. When several jars have been filled, remove the delivery tube from the water and then cease to heat the flask. Note that the gas is colourless, and that it has a somewhat ethereal smell (really due in some degree to mixture with ether vapour).

In this case the oil of vitriol seems to act as a dehydrating agent, and the change is represented by the equation—



a. Remove a jar in the usual way, place it mouth upward, withdraw the plate, and apply a flame. The gas burns freely with a strongly luminous flame, and if a little lime-water be poured into the jar and quickly

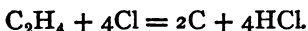
shaken up with the products of combustion, the liquid becomes turbid—thus proving the presence of carbon in the gas. The presence of hydrogen in it can be proved in the same way as in the case of marsh gas; therefore it contains carbon and hydrogen.

b. Shake a tube nearly full of the gas with some water, and note that sensible absorption occurs; in fact, 1 c.c. of water at 15° C. dissolves 0.16 c.c.

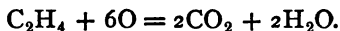
c. Repeat Experiment 254, *c*, with this gas instead of with marsh gas, and note that very little passes into the upper tube. The specific gravity is 14 ($H = 1$); therefore it is nearly of the same density as air (14.47), and much heavier than marsh gas. 1 vol weighs 14 c.grs., and the molecular weight of the body is 28, corresponding to the formula C_2H_4 . This hydrocarbon is often termed 'heavy carburetted hydrogen,' in allusion to its higher specific gravity than marsh gas; but its usual name is olefiant gas, because it reacts in the following way with chlorine.

Experiment 257.—Remove a jar of the gas from the trough, place it mouth upward, let it drain well; then remove the covering plate from its mouth and invert over it a jar of the same size full of chlorine gas, and press mouth to mouth. On standing for a short time the colour of the chlorine almost disappears, and minute *oily* drops collect on the sides of the two jars; to this oil-producing property the gas owes its name. The body formed in this reaction is commonly called 'Dutch liquid'—because first obtained by Dutch chemists—and its composition is represented by the formula $C_2H_4Cl_2$; it results from the *addition* of chlorine to the molecule. If, instea-

of proceeding as above, we mix olefiant gas with *twice* its volume of chlorine and quickly apply a flame to the mixture, a very curious combustion ensues, hydrochloric acid resulting, and a large quantity of carbon separating as dense black smoke—



Experiment 258.—Mix in a stout jar one part of olefiant gas with three of oxygen, apply a flame, and an explosion follows. In this case—



If the experiment be made in an eudiometer a contraction of one-half occurs after explosion, owing to condensation of the water produced, and the residue is found to consist wholly of carbon dioxide gas. This result confirms the conclusion already arrived at that the formula of the body is C_2H_4 .

The derivatives of this gas are very numerous, and many of them will be dealt with in Part IV., but an interesting matter remains for notice here.

There is no doubt that marsh gas acts as a *saturated* compound towards chlorine, and olefiant gas as an *unsaturated* body when tested by the same element. Moreover, for a given number of atoms of hydrogen in the molecule, olefiant gas contains twice as much carbon as marsh gas ; hence it seems to be an *addition* product from CH_4 . Now, as regards the last point, we know that no such addition is directly made to the marsh gas molecule, and the difference in condition of the two hydrocarbides admits of easy explanation if we suppose olefiant gas to contain two diad CH_2

groups united by a pair of links or bonds, while another pair is available for union with other bodies, e.g., chlorine or bromine, thus—

Marsh gas
 $\text{C}^{\text{Iv}}\text{H}_4'$

Olefiant gas
 $\text{C}^{\text{Iv}}\text{H}_2'$
 $\text{C}^{\text{Iv}}\text{H}_2'$

Chloride
 $\text{Cl}'\text{C}^{\text{Iv}}\text{H}_2'$
 $\text{Cl}'\text{C}^{\text{Iv}}\text{H}_2'$

The two hydrocarbides examined in the course of the foregoing experiments are also met with in coal gas, which may be easily prepared on a small scale, in imitation of the manufacturing process, by the following method.

Experiment 259.—Break up some coal and introduce it into a small iron retort of the form shown in

FIG. 99.



fig. 99. Connect two wash-bottles with the retort; the first, *a*, containing a very little water; the second, *b*, a mixture of 20 grams of powdered ferrous sulphate or green vitriol, with 10 grams of slaked lime, first made into a thin paste with water and exposed to the air in this condition for a few hours before use.¹ A gas delivery tube proceeds from *b* in order that the

¹ After this treatment the mixture contains hydrated ferric oxide, calcium sulphate, and excess of slaked lime.

gaseous products may be collected over water in the usual way.

Apply the heat of a Bunsen-flame or large spirit lamp to the retort, and note that gas soon distils over, and along with it vapours which condense in part in the first bottle and afford a liquid,¹ which is dark-coloured, and black oily drops of tar—coal tar—collect beneath it. The gas, in bubbling through the pasty mixture in *b*, loses much carbon dioxide, which is absorbed by the lime, and sulphur compounds removed by the ferric oxide. The gas passes on, and, having expelled the air from the apparatus, can be collected in jars or in a gas-holder. While the current of gas is still rapid, remove the delivery tube from the water, dry it, and ignite the gas as it issues ; a good bright coal-gas flame is easily obtained. The gas in the jars can be used to prove that it is lighter than air, that carbon dioxide is a product of its complete combustion, and similar experiments.

A common clay tobacco-pipe forms a capital retort if the aim is to prepare a small quantity of coal gas. Nearly fill the bowl of the pipe with fragments of coal, cover the latter with a layer of moistened clay, well pressed down by a halfpenny, secured *in situ* by wire. When the bowl is heated, gas is soon given off, and can only escape through the pipe stem, at the end of which it can be ignited.

On the large scale coal gas is generated in large earthen retorts provided with iron heads ; from these

¹ This liquid is rich in ammonia and ammonia derivatives arising from the nitrogen of the coal. The liquor is the chief commercial source of ammoniacal salts.

the gas passes into a long tube termed a *hydraulic main*, which is connected with a number of generators and catches much of the tar, thence into vessels in which it is cooled and washed with water, as in bottle *a*, and finally through lime and iron purifiers, like bottle *b*, wherein most of the carbon dioxide and injurious sulphur compounds are removed.

The purified illuminating gas obtained from good bituminous coal has the composition represented by the following analysis of a fair average sample—

One hundred volumes afforded —

Hydrogen	48.20
Marsh gas	34.26
Carbon monoxide	8.46
Carbon dioxide	2.21
Nitrogen	2.15
Oxygen	0.25
Olefiant gas and vapours of other heavy hydrocarbides }	4.47
		<hr/> 100.00

This gas, when burned at the rate of 5 cubic feet per hour, afforded a light equal to that of 16.5 sperm candles consuming 120 grains per hour.

Coals vary much in the quality of gas they afford ; thus, cannel coal—a highly bituminous kind—gives a gas which is very rich in olefiant gas and heavy hydrocarbides, and possesses high illuminating power ; by judicious mixture of this coal with inferior kinds, gas of any intermediate value can be obtained.

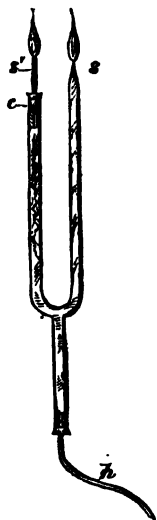
We have already learned from our experiments that the only gas present in the above mixture that br

with a strongly luminous flame is olefiant gas, and the presumption is that the proportion of this body in the gas determines its illuminating power; but the following experiment will show that the luminosity of the coal-gas flame can be caused by other bodies.

Experiment 260.—Connect the tube *b* of the apparatus, fig. 100, with a bottle evolving a steady stream of hydrogen gas, and when all air is expelled kindle the gas at the two jets *s* and *s'*; each flame is nearly colourless. Now put out the flames, remove the cork *c* carrying the glass jet, and introduce into the tube a small piece of cotton wool, as shown, moistened with a very few drops of *benzole*; insert the cork, and again kindle the gas at each jet. Note that while the flame of plain hydrogen is almost invisible, the burning gas which carries along with it the vapour of the volatile liquid hydrocarbide benzole (C_6H_6) emits a rather bright light. The luminosity in this case is evidently due to the presence of the vapour; now benzole is obtained from coal tar, and its vapour is necessarily present, even in purified coal gas; hence it contributes, as do other dense vapours, to the brightness of an ordinary gas-flame.

When coal gas is burned without previous mixture of air at any of the well-known forms of burner, soot is always deposited upon a cold surface, such as the

FIG. 100.



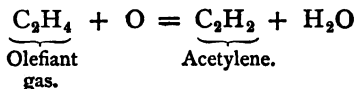
bottom of a flask or evaporating dish, if the latter be in contact with the flame. This soot is nearly pure carbon, and is evidently deposited from a portion of the flame to which the external air can have little access, else the carbon would burn to carbon dioxide gas. It can be easily seen that the portion of the flame that most readily deposits soot is the most luminous part; and it is held that the luminosity of coal gas and other similar flames is due to the intense heating either of solid carbon resulting from the decomposition of heavy hydrocarbides, or of the vapours of the latter prior to complete combustion at the outer portion of the flame, where air is in excess and can burn all into non-luminous carbon dioxide and water.

The obvious inference from these observations is that if air be mixed in sufficient proportion with coal gas prior to combustion, a colourless flame should be produced, and this is exactly the result obtained in the well-known Bunsen-burner,¹ already represented in several illustrations. If the air-holes at the base of one of these burners are closed, the flame is luminous, but when air is allowed to enter and mingle with the coal gas in the open column at the top of which the mixture burns, a colourless flame is then obtained, from which sooty particles do not separate, owing to the complete combustion of all the constituents of the gas within the solid flame, and the temperature of the latter is much higher than that of the luminous jet.

¹ Named after its inventor, Professor Bunsen, of Heidelberg.

Experiment 261.—Gradually reduce the supply of gas to a Bunsen-burner whose air-holes are fully open ; as the proportion of gas to air diminishes, a point is soon reached when the flame runs down the tube, and the gas burns at the small jet within. Note that an irritating and unpleasant smell arises, which is increased by turning on more gas ; and if a wide-mouthed flask, moistened internally with solution of cuprous chloride¹ to which excess of ammonia has been added immediately before use, be held over the burner so that the current of hot gases may come in contact with the liquid, a reddish deposit is formed on the sides of the vessel ; and this red body is found, on analysis, to contain Cu_2O , C_2H_2 . From this compound a gas is liberated on treatment with hydrochloric acid ; and this gas, named *acetylene*, has the composition C_2H_2 . One *vol* of the gas weighs 13 c.grs. ; therefore its molecular weight is 26.

This strong-smelling gas² is evidently a product of the imperfect combustion of a hydrocarbide in a limited supply of air, and its chief source in coal gas is probably the olefiant gas, which can afford it by limited oxidation, thus—

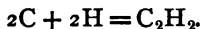


Acetylene is a frequent product of the imperfect oxidation at high temperatures of hydrocarbides rich in hydrogen, and it can not only exist unchanged at

¹ For the preparation of this solution, see p. 175.

² Acetylene is poisonous in nearly the same degree as carbon monoxide, and acts like the latter on the blood.

the enormous temperature of the electric arc, but is actually formed from its elements when the electric current is passed between carbon poles enclosed in an atmosphere of hydrogen, thus—



Acetylene is the only hydrocarbide whose *direct* synthesis has been thus effected. We need not examine this compound further at present, but pass on to the consideration of another mode of obtaining a smokeless and non-luminous gas-flame.

Experiment 262.—Obtain several pieces of wire gauze with meshes of different sizes. Hold these pieces in succession over an ordinary jet from which unignited coal gas issues, keeping the gauze about 8 or 10 centimeters (3 or 4 inches) above the jet. An inflammable—indeed an explosive—mixture of air and gas rises through the gauze; and if a flame be applied *above*, the mixture will burn with a colourless flame over the gauze, and will not ignite the mixture below, provided the meshes number at least sixty to each square centimeter. With such close gauze the heat is so rapidly conducted away by the metal (iron, brass, &c.) that the gas below does not reach a temperature sufficiently high for its ignition. If we secure the wire gauze on top of a tube of brass or iron about 5 centimeters wide and 12 c.ms. high, supported by an arm over an ordinary gas-jet, we have a convenient kind of burner for all operations requiring a large smokeless flame of moderate power, as the gas when turned on and ignited above the gauze burns quietly and steadily.

It is an obvious consequence of the principle involved in the last experiment, that a flame placed within a fine wire-gauze cage should not ignite an explosive mixture of coal gas and air outside the cage. This is, in fact, true; and finds its most important application in the coal-miner's safety-lamp invented by Sir Humphry Davy. This is nothing more than an oil lamp, the flame of which is completely covered by a wire-gauze cage, as shown in fig. 101. When this lamp is brought into an explosive mixture of marsh gas (or fire-damp) and air, the gases pass through the meshes of the gauze and burn within the cage, thus warning the miner of his danger; but the flame cannot pass *out* through the gauze for the reason already stated—a destructive explosion is thus averted, and the miner given ample time to escape from the dangerous atmosphere.

FIG. 101.



Experiment 263.—We shall now turn from the flame of coal gas to that of fat or wax gas, and our best example is a stout tallow or wax candle with a *thick twisted* wick. When the candle burns freely, it will be seen, on attentive examination, that it is but a compact gas factory. The burning wick, in the first instance, supplies the heat necessary to melt some of the wax, tallow, paraffin or other body, rich as these are in carbon and hydrogen; a little cup of molten fuel is soon formed, and from this the liquid is drawn

up into the flame by the capillary action of the wick, and there undergoes destructive distillation, and affords the gas necessary for the continuance of the combustion. In the flame itself it is easy to distinguish three zones—one dark, i.e., non-luminous—immediately surrounding the wick; outside this a highly luminous zone, and an outer mantle that emits but little light; while the base of the flame is bluish and feebly luminous. The outer zone is obviously that of complete combustion, and a cold glass or porcelain rod brought in contact with it is only bedewed with moisture but is not blackened, neither does blackening occur at the base of the flame. If, however, the rod penetrates the outer mantle and passes into the middle or luminous zone, it is quickly blackened, proving that combustion is incomplete in that portion of the flame. The inference is that the dark zone is that of unburnt gas, in which case a straight and rather narrow glass tube, held nearly vertical, and passed directly into the dark zone, should draw off combustible gas. When the experiment is made as described, mixed gas and vapour ascend the tube, and can be made to burn at the top, thus proving the correctness of our inference.

Experiment 264.—Obtain a Black's blow-pipe—a conical tin tube of the form shown in fig. 102, having a brass side tube terminating in a fine nozzle—insert the jet a short distance into the candle-flame just above the wick, and inject a steady blast¹ of air

¹ This is air taken in through the nostrils, and injected from time to time into the cavity formed by the mouth and distended cheeks. Ordinary respiration is carried on through the

from the mouth. The flame is deflected and its luminosity is much diminished, while its heating power is greatly increased. We still recognise the three zones in the blow-pipe flame, but the outer one is much extended, the middle zone is diminished,

FIG. 102.



and the inner zone, extending some distance from the nozzle of the blow-pipe, must now contain air mixed with other gases. Select a small piece of *lead-glass* tubing, and hold its point in the middle zone for a short time. Note that it is *blackened*, but the colour does not rub off, since it is due to the deoxidation, or reduction to metal, of the lead silicate of the glass by the partially burned gases of the part of the flame in which it was held; this portion is termed the *reducing* flame. Now hold the discoloured part of the glass at a short distance beyond the visible point of the flame; soon the dark colour disappears, and the glass assumes its

original appearance. This effect is due to the *oxidation* of the lead when heated strongly in a current of perfectly burned gases mixed with unchanged and hot air. Here, then, we have an *oxidising* blow-pipe flame, and these two opposite effects can be obtained at will. The blow-pipe is, therefore, a most useful instrument, and is much used in the detection of bodies nostrils without interference with the blast maintained by the mouth.

that undergo marked chemical changes under its influence. When dealing with the metals, we shall meet with many examples of its use for such purposes.

In all these cases of combustion, we have seen that flame is caused by burning *gas*. Moreover, we have learned that in the act of combustion there is always a burning body or *combustible*, and a *supporter of combustion*, and the latter has hitherto been air or a gaseous oxygen compound. But, it may be asked, are not these terms merely relative, especially when we deal with two gases? The next experiment will test this point.

Experiment 265.—Fill a jar of moderate size with coal gas by holding it mouth downwards and passing in a good stream of gas, which will displace the air. Now have a glass tube connected with a bag full of ordinary *air*, let the tube be drawn out to a fine jet, and the air-supply regulated so as to give a slow stream. Next apply a light to the mouth of the jar of gas, and while it burns, pass up through the layer of burning gas the end of the glass tube from which the fine jet of air issues; a flame is seen to proceed from the point of the tube, *the air thus burning in an atmosphere of coal gas*. This instructive and interesting experiment, then, leaves no doubt as to the answer to be given to the question just put, for it is evident that the combustible and supporter of combustion may easily be made to change places.

On comparing carbon and its compounds with silicon and its products, there are obviously many points of resemblance; moreover, neither has been

vaporised, and the atomic heat of carbon is even more irregular than that of silicon, for the weight of *diamond* that contains at 100° C. the same quantity of heat as 108 c.grs. of silver is 44 c.grs.; of *graphite* is 33 c.grs.; and of charcoal 28 c.grs., instead of 12 c.grs.¹ Thus the three forms of carbon differ amongst themselves in this respect, and are exceptions to Dulong and Petit's law (see Part I. page 58). How, then, is the value obtained that we take as the atomic weight, i.e. 12? The evidence is of the same order as that already presented in the case of silicon; that is to say, we never find *less* than twelve parts of carbon in any of its volatile compounds whose molecular weight we can determine in accordance with Avogadro's principle (see Part I. page 49), and in a large number the molecule contains *no more* than twelve parts. Further, multiples of twelve by integer numbers are alone met with, even in the more complex carbon compounds. Thus:—

Substance	Molecular Weight	Weight of Carbon in Molecule
Carbon monoxide . . .	28	12
„ dioxide . . .	44	12
Marsh gas . . .	16	12
Chloroform . . .	119.5	12
Carbon tetrachloride .	154	12
Acetylene . . .	26	24
Olefiant gas . . .	28	24
Benzole . . .	78	72

¹ Weber has recently shown that the varieties of carbon, when compared at 500° C. instead of 100° C., afford results that nearly agree with the atomic weight 12.

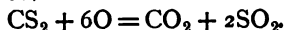
It is evident that carbon and silicon are alike tetrad or four-link elements—e.g., in CH_4 and SiH_4 , CCl_4 and SiCl_4 .

Again, carbon dioxide and silicon dioxide are anhydrides of acids which are alike feeble and easily decomposed by heat, yet the metallic salts derived from these acids are in most instances capable of withstanding very high temperatures unchanged, though chemical agents readily displace the acids from the bodies referred to.

It may be added that carbon and silicon appear to perform complementary parts in nature, since the former element is chiefly concerned in the structure and processes of animal and vegetable life, while silicon is almost exclusively confined to the mineral kingdom, in which it plays a highly important part, and forms about one-third of the solid crust of the globe.

Experiment 266.—Pour a few drops of the liquid ‘bisulphide of carbon’ into the spoon used in Experiment 169. Note that the liquid quickly evaporates, owing to its high volatility; while the compound, as commonly sold, diffuses an unpleasant smell. Bring a flame to the liquid, and the latter burns; now plunge the spoon into a jar of air, and allow the combustion to proceed for a short time; withdraw the spoon, and cover the jar with a glass plate. Add some lime-water to the contents, and note the turbidity produced, indicating the production of carbon dioxide, while the strong smell of burning sulphur is perceived. The liquid has the composition represented by the formula CS_2 , and when burned it affords the

products of the combustion in oxygen (*vide* Experiments 58 and 59) of the two elements, viz. :—



Carbon disulphide is not conveniently prepared on the small scale, but it is made in large quantities by passing the vapour of sulphur over red-hot coke ; the two elements unite, and the product, when condensed, is a colourless, highly refractive liquid, heavier than, and nearly insoluble in, water (specific gravity 1·29), and boiling at 46° C. No lower sulphide of carbon has yet been formed.

Test the solubility of the following bodies in the liquid : Caoutchouc, iodine, fat, and resin. Note that it dissolves these with ease : in fact, the commercial disulphide is chiefly employed in the arts as a solvent for these bodies, and, as we shall find later on, for sulphur and for waxy phosphorus. Carbon disulphide mixes with alcohol, chloroform, and benzole ; and though almost insoluble in water, dissolves in solution of alkaline sulphydrates—e.g., potassium sulphydrate, KSH, and forms therewith a sulphocarbonate— K_2CS_3 —analogous to the common carbonate— K_2CO_3 . Hence, CS_2 is to be regarded as the sulphur analogue of CO_2 .

CYANOGEN.—Carbon forms an important and highly poisonous compound with nitrogen, termed *cyanogen*— CN —a body which acts as a monad radicle, and forms, with ordinary metals, a class of salts termed cyanides, and with hydrogen the deadly prussic acid—HCN.

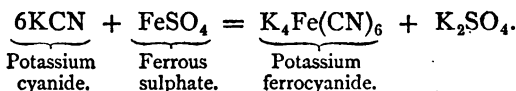
When ammonia gas is passed over carbon heated to a high temperature in a porcelain tube, one atom

of carbon takes the place of two atoms of hydrogen in ammonia, and the compound HCN is formed ; but this body is prussic acid, *i.e.* *hydrocyanic* acid or hydrogen cyanide, and immediately unites with a molecule of ammonia, forming therewith NH_4CN , or ammonium cyanide. If the carbon be impregnated with potassium carbonate and then heated in a current of ammonia, or even of nitrogen gas, the compound KCN is produced. This is obviously the potassium salt of the same acid, or *potassium* cyanide.

Any organic matter containing nitrogen can be made to afford potassium cyanide when heated with potassium or its carbonate.

Experiment 268a.—Break up into very small pieces some glue or gelatine in a perfectly dry condition. Take a dry tube of hard glass closed at one end, and introduce a little of the glue ; then add a clean piece of metallic *potassium* about the size of half a pea and cover it with more of the powdered glue. Now heat the contents of the tube to low redness, and continue the heat until vapours cease to be evolved and only a carbonised mass remains in the tube. Allow the contents to cool, then break the tube, and throw the fragments with the charred residue into a little cold water in a porcelain dish. If any free potassium is in the tube it will burn when added to water, so that the addition must be carefully made. When all action is over, stir up the mixture and filter from the charcoal and glass. The solution should be nearly colourless and alkaline to test-paper ; it contains potassium hydrate and carbonate with some potassium *cyanide*.

In order to recognise the cyanide, add to the clear liquid in a test-tube two or three drops of a solution of *ferrous sulphate*, and warm the turbid mixture that results. The following change takes place—



The new compound formed is in solution, and it would be possible to crystallise it out on evaporating the liquid ; but this is not necessary in order to detect its presence, since, when treated with an iron salt in *acid* solution, it can afford a beautiful precipitate of 'Prussian blue,' and a drop of ferric chloride followed by an excess of hydrochloric acid at once develops that characteristic colour.¹ We thus learn (*a*) that the well known pigment 'Prussian blue'² can be formed by the action of a *ferric* salt on potassium ferrocyanide ; (*b*) that the latter is formed when a *ferrous* compound acts on potassium cyanide ; and (*c*) that the cyanide is formed when nitrogenised organic matter is heated with potassium. The whole chain of operations forms Lassaigne's useful and instructive *test for nitrogen in organic compounds*.

Potassium ferrocyanide, or 'yellow prussiate of potash,' is manufactured in very large quantities by a method which is similar in principle to that just carried out. Waste nitrogenous organic substances—*e.g.* bone shavings, dried blood, glue waste,

¹ Addition of acid alone is generally sufficient, as the excess of iron salt added in the second stage affords sufficient ferric compound when the acid is added.

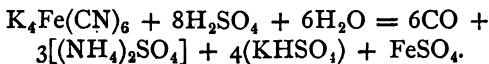
² The empirical formula of the Prussian blue formed by the action of a ferric salt on the ferrocyanide is $\text{Fe}_7(\text{CN})_{14}$.

&c.—are mixed with potassium carbonate and scrap iron, and the mixture is heated in iron vessels, which are made to revolve in order to mix the materials. After sufficient heating, the mass is allowed to cool, then extracted with water, filtered, and the solution evaporated. The ferrocyanide separates on cooling, and when purified by recrystallisation affords beautiful yellow tabular crystals, which are soluble in about three parts of water. It consists of $K_4Fe(CN)_6 \cdot 3H_2O$. The three molecules of watery crystallisation are easily driven off by gentle heat, and the anhydrous salt left.

Experiment 266b.—To a saturated aqueous solution of the ferrocyanide add some strong hydrochloric acid followed immediately by *ether*. A precipitate forms of the acid $H_4Fe(CN)_6$, which is white at first, but is very unstable, and rapidly becomes blue owing to decomposition.

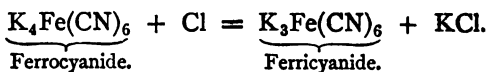
Experiment 266c.—Add a solution of the ferrocyanide to a solution of *ferrous* sulphate, and note that a nearly white precipitate is formed; but this precipitate rapidly becomes blue on exposure to the air. The white precipitate contains $K_2Fe''Fe(CN)_6$, and the blue body formed on oxidation is another variety of Prussian blue, whose formula is $K_2Fe_4(CN)_{12}$.

Experiment 266d.—Heat a few fragments of the ferrocyanide with a little *strong* sulphuric acid in a test-tube. CO gas is evolved, and can be ignited at the mouth of the tube. This method is the best for the preparation of pure CO. The change is thus expressed—



Experiment 266e.—Pass chlorine gas into a solu-

tion of potassium ferrocyanide in water. Note that the colour of the liquid deepens, and if a drop be removed from time to time and tested with *ferric* chloride, the amount of blue precipitate formed by the first few drops is seen to diminish in those which succeed,¹ and when the action of chlorine is complete the liquid no longer gives a blue precipitate with a ferric salt.² But a portion of the solution added to ferrous sulphate or other *ferrous* salt causes a *deep blue* precipitate at once. The compound which gives these reactions can be separated, on evaporating the solution, in beautiful ruby red crystals of *potassium ferricyanide*, or red prussiate of potassium, which contain $K_3Fe(CN)_6$.³ The action of chlorine on the ferrocyanide may be thus expressed—



When purified by recrystallisation, the salt gives with silver nitrate a reddish precipitate of $Ag_3Fe(CN)_6$.

If potassium ferrocyanide be digested with slightly diluted nitric acid a new salt results, *potassium nitro-prusside*, $K_2Fe(CN)_5NO$, which may be regarded as a nitro-substitution product from the ferricyanide. This compound is used in testing for alkaline sulphides (see p. 214).

We now return to the ferrocyanide, in order to examine products of the disruption of its molecule.

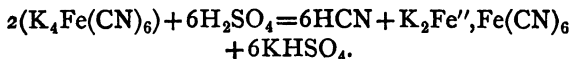
Experiment 266 f.—To a solution of the ferrocyanide contained in a test-tube add half its volume

¹ See Part III. p. 186.

² *Ibid.*

³ It is probable that the above formula should be doubled, thus— $K_6Fe_2(CN)_{12}$.

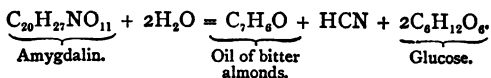
of diluted sulphuric acid, and heat. Note that the liquid becomes bluish, and soon a bluish-white compound separates, which is potassio-ferrous ferrocyanide, $K_2Fe'', Fe(CN')_6$, while an odour is perceived resembling that of 'bitter almonds.'¹ This is the odour of hydrocyanic or prussic acid; *the utmost care should be taken to avoid inhaling the deadly poison*, and all experiments with it should be conducted near to a flue with a good draught.² The reaction that occurs in the tube is—



If a cork be fitted to the mouth of the test-tube, and it is provided with a glass tube bent twice at right angles, like that for gas delivery, the hydrocyanic acid can be distilled over into another tube containing a little water to condense the vapour, and a very dilute and faintly acid solution can be prepared in this way.

This is the method directed in the B.P. for the

¹ Bitter almonds contain a crystalline principle termed 'amygdalin,' which, under the influence of a body named 'emulsin,' best obtained from *sweet* almonds, undergoes decomposition into hydrocyanic acid, oil of bitter almonds, and a variety of sugar called glucose—



Hydrocyanic acid is also present in 'laurel water' obtained by distilling laurel leaves with water.

² Inhalation of the vapour is extremely dangerous, as a very small quantity of the poison acts with great rapidity. For antidotal treatment see p. 208.

preparation of the dilute acid used in medicine, which contains only 2 per cent. of real HCN. With a solution prepared as described, or with small successive quantities of the Pharmacopœial acid, make the following observations :

a. Note the *odour*, and hold over the liquid a piece of white filtering paper which has been first soaked in a solution of *guaiacum* resin in spirits of wine, then dried and moistened with a very dilute aqueous solution of copper sulphate. The paper assumes a distinct *blue* colour in the vapour of prussic acid. This is Schönbein's test for the acid.

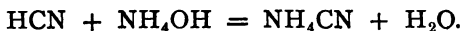
b. Add silver nitrate solution to another portion, and note that a white precipitate is formed. This consists of AgCN , which is insoluble in cold nitric acid, but is slowly soluble in the hot acid.¹ The silver cyanide is sparingly soluble in ammonium hydrate.

c. To another part add excess of caustic potash, then a drop or two of ferrous sulphate solution, warm the turbid mixture and, without filtration, add excess of hydrochloric acid. Note that a Prussian blue separates. Its formation is due to the series of reactions already pointed out in Experiment 266*a*.

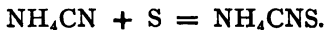
d. Mix a few drops of ammonium hydrate and then of *yellow* ammonium sulphide with some of the

¹ The silver cyanide is easily soluble in solution of potassium cyanide, a soluble double cyanide, $\text{AgK}(\text{CN})_2$, being formed. This body, and many other double cyanides of which it is a type can be easily decomposed by dilute acids, unlike the special group of compound cyanides of which potassium ferrocyanide is the type.

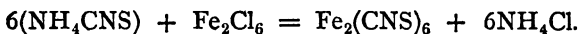
acid in a test-tube ; then pour the yellow mixture into a small porcelain capsule, and very slowly evaporate to dryness to expel the excess of sulphide, but take care not to heat the residue strongly, else it may be decomposed. Then add a few drops of water to dissolve the residue, and a drop of *ferric* chloride, when a fine *blood red* colour is developed, which can be discharged by a few drops of mercuric chloride. The following reactions occur in the course of the above treatment. Firstly, ammonium cyanide is formed—



Then the cyanide unites with an atom of sulphur obtained from the sulphide and forms ammonium *sulphocyanate*, or thio-cyanate—

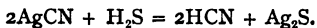


The latter reacts with ferric chloride and forms the blood-red coloured *ferric sulphocyanate*,¹ thus—



This is Liebig's test for prussic acid, and is very delicate.

In the *b* test with silver above described a quantity of silver cyanide is formed ; this should be collected on a filter, washed with water, and thoroughly dried. Anhydrous hydrocyanic acid can be prepared from this body by passing sulphuretted hydrogen gas over it, when—



The anhydrous acid is a most *deadly poison* ; it is a colourless liquid of specific gravity 0.706 ; it boils at 21° C., and affords a

¹ A ferrous salt, if pure, does not give any colour with a thio-cyanate.

combustible vapour. *Its preparation should on no account be attempted by the student.* By the action of chlorine on hydrocyanic acid a cyanogen chloride is formed, CNCl , which is a gas at ordinary temperature, but a liquid at 11°C . A solid chloride is also known which is a polymer of the first, and contains $\text{C}_2\text{N}_2\text{Cl}_3$.

We can also obtain *cyanogen* itself from its silver salt, and without danger, if a very small quantity be treated as in

Experiment 266g.—Introduce a little of the perfectly dry silver cyanide into a very narrow tube of hard glass closed at one end. Heat the tube at first just above the silver salt, and then heat the latter; decomposition soon takes place, and a gas issues which is easily kindled at the mouth of the tube, where it burns with a beautiful rosy flame. This gas is *cyanogen* separated from the metal, which latter remains in the tube.¹ The specific gravity is 26 ($\text{H}=1$); therefore its molecule contains the group CN *twice*, and is thus constituted like the molecule of an *elementary* gas such as chlorine; indeed, cyanogen resembles chlorine in its *monad* character, in its attraction for silver, and in forming potassium and sodium salts which present much chemical similarity to the corresponding compounds of chlorine with those metals. The cyanogen group is often indicated by the symbol Cy' instead of CN .

Potassium cyanide can be obtained by neutralising

¹ If mercuric cyanide be heated instead of the silver compound a similar decomposition occurs, but a brownish body is left in the tube, named *paracyanogen*, which is probably a polymer of cyanogen.

hydrocyanic acid or by the synthetic process described at first, but it is most conveniently prepared for use in the arts from the easily obtained ferrocyanide. It is employed largely in electrotyping, for cleaning the precious metals, and as a solvent for silver salts in photography.

Experiment 266 h.—Mix perfectly dry potassium ferrocyanide with half its weight of dry potassium carbonate, and heat the mixture to fusion; the mass becomes black, owing to the separation of iron and a carbide of iron, which sink. If the liquid be kept fused for some time the iron subsides, and a clear liquid can be poured off and allowed to solidify on a cold iron plate. It must be quickly broken up and kept in a stoppered bottle, as it is very deliquescent, and is partially decomposed even by the carbon dioxide of air, with evolution of hydrocyanic acid. This salt is highly poisonous, though the compound from which it is derived—the ferrocyanide—is non-poisonous. It gives off hydrocyanic acid when treated with hydrochloric, sulphuric, or other acid.

Potassium cyanide is a powerful deoxidising agent, as it can readily unite with an atom of oxygen, and form KCNO, or potassium cyanate; thus, when fused with lead oxide metallic lead is obtained—

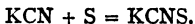


Cyanic acid is only obtained in the free state with much difficulty, as it quickly changes into one of two polymers, according to circumstances—into *cyamelide* or into cyanuric acid, $\text{H}_2\text{C}_2\text{N}_2\text{O}_3 = (\text{HCNO})_3$. Fulminic acid, the silver and mercury salts of which constitute the fulminating compounds used in percussion caps and detonators generally, is metameric with

dicyanic acid, $\text{H}_2\text{C}_2\text{N}_2\text{O}_2$, and fulminuric acid with tricyanic or cyanuric acid.

Ammonium cyanate is remarkable, as it is metameric with *urea*, CON_2H_4 , into which it is easily converted by heating to 100°C . (Wöhler).

Just as potassium cyanide can combine with oxygen and form the cyanate, so can it unite with sulphur, when fused with that element, and afford the analogous *sulphocyanate* or *thio-cyanate*—



We have already formed ammonium thio-cyanate in the course of testing for hydrocyanic acid (see p. 205), and produced from it the magnificently-coloured ferric thio-cyanate in the course of the same operation.

When ammonium thio-cyanate is heated to a temperature of 170°C ., it affords the metameric body thio-urea, CSN_2H_4 —the sulphur analogue of ordinary urea (Reynolds).

Treatment of Poisoning by Prussic Acid.—This poison is so rapid and deadly in its action that there is little time for the administration of antidotes. Inhalation of vapour of *ammonia* as a stimulant is to be immediately resorted to. If the patient is partially or wholly insensible, cold water must be dashed over him and stimulants administered. With a view to form inert Prussian blue in the stomach, administer a solution of iron sulphate to which has been added a little ‘muriate tincture of iron.’ This solution should be followed, after a minute or so, by a dilute solution of potassium or sodium carbonate.

CHAPTER XXII.

EXPERIMENTS WITH SULPHUR AND ITS COMPOUNDS.

SULPHUR = 32.

Experiment 267.—Powder a small quantity of ‘iron pyrites’— FeS_2 ; introduce it into a long narrow tube of hard glass closed at one end, and heat gently at first but afterwards to redness. Note, that as the temperature rises, the cool sides of the glass tube in front of the hot mineral become coated with yellowish matter; and this, if heated, is seen to melt to a reddish-brown liquid. This body is the volatile element SULPHUR, separated by heat from the pyrites; but the iron residue retains some sulphur, even after prolonged heating out of contact with air, and the composition of this residue is nearly represented by the formula Fe_3S_4 . The change that occurs on heating, therefore, may be expressed by the equation—



The residue, unlike the body from which it is obtained, is attracted by the magnet; and, consequently, is termed magnetic pyrites.

The sulphur prepared in this way is found to possess the same general properties as that met with

in the free state in nature, for the element occurs in various volcanic districts, as that of the Solfatara, near Naples; and our chief supplies are drawn from these sources. Although compounds of sulphur are widely diffused in nature, the crude native material is the chief source of the two forms of sulphur met with in commerce—viz., roll and flour of sulphur. The mode of obtaining these may be thus briefly described:—

The mixture of sulphur, with earthy and other impurities, is placed in a pit along with a small quantity of fuel, which is then fired. When the temperature is sufficiently raised, the mass is covered up, and the whole allowed to smoulder; the sulphur melts, and collects on the floor of the pit. This crude sulphur is converted into 'flour' and 'roll' by distilling from an iron retort into a large brick chamber, the impurities are left, while the vapour condenses rapidly and falls, at first as a fine yellow powder, or 'flour of sulphur,' which is removed. Later on the chamber becomes so hot that the sulphur condenses in the liquid form, and collects on the floor, whence it can be drawn off into cylindrical moulds, in which it solidifies on cooling, and forms the 'roll brimstone' of commerce.

A nearly white variety of sulphur used in medicine is termed *lac sulphuris*, and will be prepared in Experiment 288.

Experiment 268.—Introduce into a Florence flask 10 or 15 grams of roll sulphur, or 'cane brimstone,' in coarse powder, heat over a Bunsen-flame, and observe that the sulphur soon begins to melt;

and when completely liquefied (at 115° C.), it may readily be shaken about in the flask, owing to its easy mobility. On continuing the application of heat, a remarkable change is soon noticed, for the liquid 'thickens,' and the sulphur becomes so *viscid* (at 220° C.), that the flask may be inverted without spilling any of its contents. Further heating renders the body somewhat more mobile, especially as the boiling-point (446° C.) is approached; then much sulphur vapour, of a reddish-brown colour,¹ is evolved. When the boiling-point is reached, pour the molten sulphur carefully and rather slowly out into a considerable quantity of cold water; then pour away the water and examine the cold sulphur. Note that the element, as thus obtained, is no longer a hard, yellow, and opaque crystalline solid, but is a soft, elastic, translucent body—evidently uncrystalline and *amorphous*—which may be drawn out into strings or moulded into various shapes. The element in this condition is termed 'plastic sulphur,' and is used for making moulds of coins, &c. Dry the plastic sulphur thus obtained, and preserve for some time. Note that it gradually loses its translucent appearance, and ultimately becomes opaque and brittle like the roll sulphur from which it was produced.

¹ The specific gravity of this vapour near to the boiling point is 95.5 ($H = 1$), but at a temperature of 900° C. the specific gravity is 32.1. Therefore, while at high temperatures the gaseous molecule of sulphur contains two atoms (each having the atomic weight 32), at temperatures near to the condensing point the molecule is much more complex, and contains *six* atoms of the element.

Experiment 269.—Heat a small quantity of roll sulphur in a test tube until it is just melted, and then pour it out into water as before. Note that the sulphur thus obtained is of the same colour, and as hard and brittle as the roll sulphur, and is therefore quite unlike that obtained by rapid cooling from a much higher temperature ; moreover, when broken it is distinctly *crystalline* in appearance.

Experiment 270.—Take three test-tubes and fill each about one-third with carbon disulphide. Introduce into one of these tubes (*a*) a piece of roll sulphur about the size of a small pea, into another (*b*) about the same weight of fresh *plastic* sulphur, and into the third (*c*) some ‘flour of sulphur.’ Agitate each tube occasionally, and note in the case of—

a. That the roll sulphur in this tube has completely dissolved, and that when some of the solution is poured out on a glass plate the very volatile solvent quickly disappears and leaves the sulphur behind in the form of distinct yellow crystals. Therefore roll sulphur is soluble in this particular liquid, and is deposited therefrom in the crystalline form on evaporation.

b. That the plastic sulphur does not seem to dissolve, and some of the liquid evaporated on a glass plate does not leave any residue. Therefore plastic or non-crystalline sulphur is not soluble in carbon disulphide, and in this, as in the other characters observed, differs widely from the crystalline variety of the element.

c. In this case there is little evidence of solution, as the powder is diffused through the liquid ; hence

we must filter in order to ascertain whether any sulphur has been dissolved. Pour the contents of the test-tube on a *dry* filter and allow some of the liquid that passes through to fall on a glass plate. Evaporate as before, and note that yellow crystals separate which can only have been obtained from the material used, while the powdery residue on the filter cannot be dissolved by any amount of the disulphide, and when examined with a lens or microscope is devoid of any trace of crystalline structure. Therefore flour of sulphur consists of a finely-divided mixture of two varieties of the element easily recognised—one being soluble, the other insoluble, in carbon disulphide. Thus again, in the case of sulphur, we have evidence of the allotropism already noted in our examination of carbon and of oxygen.¹

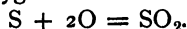
Experiment 271.—Melt cautiously in a large porcelain crucible some roll sulphur, but avoid combustion of the element or allowing the temperature to rise so high as to induce the viscid condition. When completely melted, let the mass slowly cool, and when a firm crust has formed on the surface pierce the crust in two places, and pour out into water from one of the holes the still molten sulphur from within. When quite cold the hollow mass of sulphur can be removed from the crucible, and when the crust is now completely removed the cavity will be found studded with beautiful long needle-like crystals of the element. This experiment is a case of *crystallisation from fusion*.

It may be added that in native sulphur and that

¹ Other, but less important, allotropic varieties of sulphur have been obtained.

crystallised from solution in carbon disulphide the element assumes the form of a short *rhombic* octohedron, while the sulphur rapidly crystallised from fusion separates in long prisms derived from the *monoclinic* system.

Experiment 272.—Heat a small fragment of sulphur on an iron spoon. Note that combustion soon begins, the sulphur burning with a blue flame, while a suffocating gas or vapour, similar to that of a burning sulphur match, is produced. If the still burning sulphur be plunged into a jar of oxygen, as in Experiment 59, the combustion becomes much more energetic, and the blue flame more brilliant, but we do not observe any other change, and the sulphur burns completely away without leaving any solid or liquid residue. Therefore sulphur combines with oxygen, either pure or diluted, as in air, and produces a gaseous or vaporous oxide. By a method analogous to that employed in the case of carbon (see page 146) it has been found that for every 32 c.grs. of sulphur burned, 64 c.grs. of the gaseous oxide are produced; therefore one atom of sulphur unites with two of oxygen, and forms sulphur dioxide, which contains its own volume of oxygen—

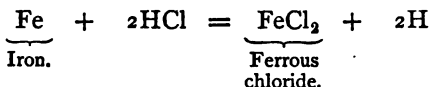


We shall postpone for a short time our study of the compound thus obtained, and revert to one of the earliest experiments we made, namely, that in which we heated iron filings and sulphur together (Experiment 11) and formed a compound of these elements.

Experiment 273.—Repeat Experiment 11, using 32 grams of sulphur for every 56 grams of iron—

atomic proportions—and heat strongly in a fireclay crucible instead of a glass tube, until a semi-fused mass is obtained. The product has the composition represented by the formula FeS , and it is termed *ferrous sulphide*.

Experiment 274.—Introduce into a test-tube containing some dilute hydrochloric acid a few fragments of metallic iron; effervescence soon begins, and the gas evolved can be burned at the mouth of the tube, and its characters proved to be those of hydrogen. This hydrogen results from the following reaction:—



Experiment 275.—Make a similar experiment with a few fragments of the ferrous sulphide prepared in Experiment 273. Note that gas is evolved in this case also without the aid of heat, but, unlike hydrogen, it has a most offensive smell, resembling that of rotten eggs, and when burned at the mouth of the tube produces a gas having the suffocating odour of that obtained when sulphur burns in air. Therefore the gas evolved contains sulphur, and the last experiment would lead us to suspect that it is a compound of sulphur with hydrogen.

SULPHURETTED HYDROGEN (H_2S). 1 Vol weighs
17 c.grs. Molecular weight = 34.

Experiment 276.—Fit up a gas evolution apparatus as in fig. 103. The bottle *b* should contain a little water wherewith to wash the gas produced in *a* from

impurities. Introduce into *a* some fragments of ferrous sulphide, then enough water to cover them, and, having inserted the cork, pour some strong commercial hydrochloric acid or sulphuric acid down the funnel tube. Gas is soon evolved, and, after the

FIG. 103.



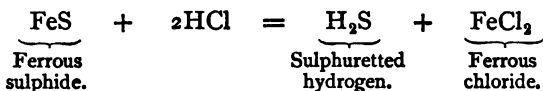
expulsion of the air from the apparatus, can be collected from the tube over water;¹ but it is advisable to use a small porcelain basin as a pneumatic trough rather than one of painted metal, as the gas discolours most paints and acts on the metal. Collect a jar of the gas, and note that it is colourless, and possesses the unpleasant smell already noticed, that it burns when a flame is brought to the mouth, and during its combustion a little yellow sulphur separates on the side of the jar.

Fill another jar with the gas, remove from the trough, and, holding the tube mouth upwards, then attempt to pour the gas into another and a dry tube containing only air, and similarly placed beside that containing the gas. After pouring, bring a flame to the mouth of the second tube, and note that its contents are combustible, proving the greater density of the gas than air. Note also that moisture is deposited on any cold surface brought over the burning gas, and it can be proved, as in the case of hydrogen, that this

¹ Though very sensibly soluble, see p. 221.

Experiments with Sulphuretted Hydrogen. 217

is water, produced even when the carefully dried body is burned. Therefore it contains hydrogen as well as sulphur. The specific gravity of the gas is 17, and 1 vol weighs 17 c.grs; hence its molecular weight is 34, and this is the molecular weight of a compound of one atom of sulphur (32) and two of hydrogen. This gas is termed *sulphuretted hydrogen*, and its formula is H_2S . The reaction by which it is formed may be thus written :—

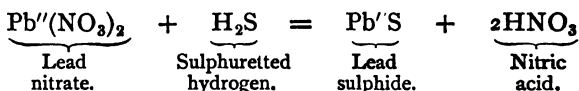


Although sulphuretted hydrogen is a gas at ordinary temperature and pressure, it can be reduced to a colourless liquid by a pressure of 17 atmospheres at 10°C . The gas can be obtained by the action of acids on other sulphides than that of iron—for instance, by heating native antimony sulphide with hydrochloric acid; and this source affords sulphuretted hydrogen in a pure condition and unmixed with free hydrogen.¹ The gas is met with in nature in volcanic districts and in certain mineral waters, as those of Harrogate, Aix-la-Chapelle, &c. It is a frequent product of decomposition of organic bodies containing sulphur, and is therefore met with in the gaseous products of putrefaction of animal matters, such as white of egg, which contain the element in question.

Experiment 277.—Soak a piece of bibulous paper in a solution of *lead* nitrate or acetate, and hold the moist slip over the delivery tube or the test tube used

¹ $\text{Sb}'''\text{S}_2 + 6\text{HCl} = 2\text{SbCl}_3 + 3\text{H}_2\text{S}$.

in Experiment 275. Note that the portion of the paper moistened with lead salt is immediately blackened. This change is due to the combination of the sulphur with lead, and the consequent production of lead sulphide—PbS—which is of a dark colour.¹ The following equation represents the change that occurs:—



This lead paper serves as a most convenient test for the presence of sulphuretted hydrogen in any gaseous mixture, and it is important to be provided with so simple a test, because sulphuretted hydrogen is a poisonous body. When inhaled in the pure state it acts rapidly as a narcotic poison ; but when present in air to the extent of about 6 per cent. it acts as a narcotic-irritant poison ; if present in still smaller proportion it causes nausea, headache, and diffused pains over the abdomen. It is therefore a gas which should be inhaled as little as possible during chemical operations. Where symptoms of poisoning appear, Taylor recommends immediate removal to pure air, dashing cold water over the face, and the cautious inhalation of the stimulant vapour of ammonia.

Sulphuretted hydrogen often arises from drains, and if such effluvia escape steadily into a dwelling-house the health of the inhabitants is seriously endangered. Lead-paper serves as a safe index of the purity of the atmosphere in this respect, for a piece of the paper exposed to the air of a room will

¹ The discoloration of lead paint is due to the same cause.

be slightly discoloured *after ten minutes* if any sensible traces of sulphuretted hydrogen are present.

Experiment 278.—Take five test glasses or tubes ; introduce into one a small quantity of solution of copper sulphate ; to another solution of tartar emetic (antimony and potassium tartrate), to which enough hydrochloric acid has been added to redissolve the white precipitate formed on first adding the acid ; to another solution of zinc sulphate, to which some hydrochloric acid has been added ; to another iron sulphate solution (green), similarly acidulated ; to another potassium sulphate. Pass some sulphuretted hydrogen gas through each solution. Note the results as follows—

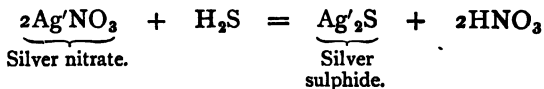
- | | | |
|--------------------|---|--------------------|
| 1. Copper solution | . | Black precipitate |
| 2. Antimony „ | . | Orange precipitate |
| 3. Zinc „ | . | No change |
| 4. Iron „ | . | No change |
| 5. Potassium „ | . | No change |

Now add a few drops of NH_4OH to Solutions 3, 4, and 5 ; and note that in 3 a *white* precipitate is formed in quantity, in 4 a *black* precipitate appears on rendering the liquid alkaline, and no change is observed in 5. Each body precipitated is a compound of sulphur with the particular metal, and the various metals may be divided into three great classes, according to the action of their solutions with sulphuretted hydrogen, viz.—(a) those whose sulphides can be formed in *acid* solutions, because insoluble in such liquids, like copper and antimony ; (b) those whose sulphides are *not* formed in acid solutions—

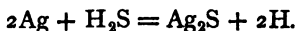
because soluble in them, but which are produced in *alkaline* liquids; and (*c*) those whose sulphides, if formed in solution at all, are soluble in acid, alkaline, and neutral liquids.

Advantage is taken of these facts in the analysis of metallic compounds—a subject that will be dealt with in some detail in Part III.

Experiment 279.—Moisten some bibulous paper with a solution of silver nitrate and expose it to the action of the sulphuretted hydrogen gas. Note that the paper is blackened, as in the case of that moistened with lead nitrate in Experiment 277, and when the black body is analysed it is found to consist of silver sulphide, $\text{Ag}'_2\text{S}''$; therefore the change may be represented by the equation—



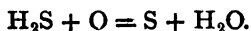
Experiment 280.—Expose a silver coin, or pure silver leaf, to the action of the gas, and note that blackening occurs in this case also, evidently owing to the combination of the metal with the sulphur, and its consequent removal from the gas—



Many other metals—lead and tin, for example—remove sulphur from the gas, especially if gently heated in it, and when the process is conducted in closed vessels the residual hydrogen is found to occupy the *same space* as the gas from which it was derived; this observation evidently confirms the con-

clusion already drawn from the specific gravity of the gas—viz., that its molecule contains two atoms of hydrogen and one of sulphur. It is interesting to note that the sulphur atom acts as a diad in sulphuretted hydrogen, H_2S , just as oxygen does in water, H_2O ; in fact, the two compounds are evidently analogous bodies so far as constitution is concerned, and sulphuretted hydrogen may be spoken of as the sulphur analogue of water, just as carbon disulphide is the sulphur analogue of carbon dioxide.

Experiment 281.—Fill a jar with gas by downward displacement of air, remove the gas delivery tube; quickly introduce some water into the jar, close its mouth with the hand, and shake. Note that absorption takes place, indicating that the gas is soluble in water, and the solution has a *faint acid* reaction. As a matter of fact, 1 c.c. of water at 15°C . is found to dissolve 3.23 c.cs. of the pure gas. The saturated solution in water can be easily prepared by passing a current of the gas through water, with occasional agitation of the liquid, until the bubbles cease to diminish in volume in their transit. The liquid thus obtained smells strongly of the compound, and if used instead of the gas in Experiment 278 will be found to afford the same results; hence it is frequently substituted for the gas in chemical testing. When this solution is allowed to stand for some time it becomes somewhat milky in appearance, and loses its smell, owing to the separation of sulphur, as the result of the partial oxidation of the sulphuretted hydrogen by the oxygen of air in contact with the water, thus—



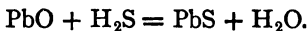
Experiment 282.—Fill a jar with sulphuretted hydrogen, and another of the same size with chlorine gas, prepared as in Experiment 139. Close the mouth of each jar with a glass plate, then bring that of the chlorine jar over the other; remove both plates, and allow the gases to mingle. Note that decomposition immediately takes place, and yellow sulphur separates on the sides of the jars, while the odour of sulphuretted hydrogen disappears, and a smell of hydrochloric acid gas is developed instead. The change is represented by the following equation, and is due to the attraction of chlorine for hydrogen—



This experiment at once suggests a mode of deodorising an atmosphere rendered offensive by sulphuretted hydrogen gas; but the most convenient source of chlorine evidently is 'chloride of lime,' or bleaching powder, as this body, when acidulated, as in Experiment 150, with any acid (such as common vinegar, diluted acetic acid), evolves chlorine gas. When the solution of bleaching powder, or some of the solid diffused through a little water, is exposed on plates in a confined space, and some vinegar added, the smell of sulphuretted hydrogen (and of certain other offensive sulphuretted compounds) is soon removed.

Similar experiments can be made by adding some solution of chlorine, iodine, or bromine to sulphuretted hydrogen water; hydrochloric, hydriodic, or hydrobromic acids are formed, and sulphur separates and can be filtered off; dilute solutions of the two last-named acids are often prepared in this way.

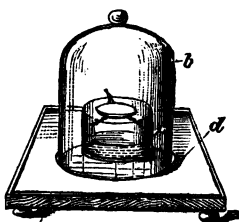
Experiment 283.—Shake up some sulphuretted hydrogen water with *litharge* or lead oxide, PbO , and note the black lead sulphide produced, and the removal of the smell of the H_2S , but no gas is evolved. In this case the metal removes the sulphur, as in former experiments, and the oxygen previously united with the metal oxidises the hydrogen of the gas, and water results; hence the absence of any gaseous product of the reaction—



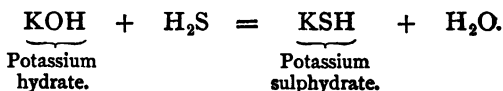
The result is analogous to that obtained when a copper oxide is acted upon by an unoxidised acid (see Experiment 132), and leads us to examine the effect of an alkaline hydrate upon the gas, as we have already found that the solution of the H_2S in water, when tested, gives a distinct but feeble *acid reaction*.

Experiment 284.—Half fill a large test-tube with a strong solution of potassium hydrate, and pass sulphuretted hydrogen gas through the liquid until it ceases to dissolve. Note that a very large quantity of gas must be passed before the liquid is saturated and the smell of the gas is perceived; this is presumptive evidence that the solution is due to chemical change. Now pour out a portion of the solution into a watch-glass, and support the latter on a wire triangle, as in fig. 104, over some oil of vitriol

FIG. 104.



contained in the vessel *c* ; then cover the whole with the glass bell-jar *b*, whose mouth should rest airtight on the ground-glass plate *d*. Slow evaporation takes place in this so-called *desiccator*, the aqueous vapour arising from the solution being absorbed by the oil of vitriol in *c*, and colourless crystals soon make their appearance. These crystals, when analysed, give results that lead to the formula $2(\text{KSH}), \text{H}_2\text{O}$. These crystals, when heated to 200°C ., lose water, and the compound KSH, termed potassium sulphhydrate, remains. Consequently the action of sulphuretted hydrogen on potassium hydrate is represented by the following equation—



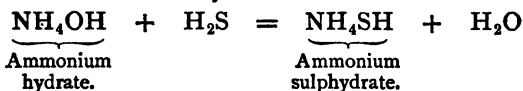
The body formed is therefore analogous to caustic potash, the oxygen of which has been displaced by the sulphur of the H_2S ; but the group SH is evidently more distinctly acidic than OH.

Experiment 285.—Add a few drops of the solution produced in the last experiment to some water contained in a white evaporating dish, and then pour in some solution of sodium nitro-prusside ($\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$). Note that a beautiful but very evanescent bluish-purple colour is developed.

Apply the same test to some sulphuretted hydrogen water, and to a portion of the pure caustic potash solution. In neither case is any colour produced ; therefore the nitro-prusside serves to distinguish the

alkaline sulphhydrate, or, it may be added, any alkaline sulphide.¹

Experiment 286.—Take about 20 c.cs. of ammonium hydrate solution, dilute it with about four times its volume of water, and saturate the liquid with sulphuretted hydrogen gas. The latter dissolves in large quantity, and a few drops of the solution diluted with water and tested with nitro-prusside afford the colour reaction already observed. In this case—



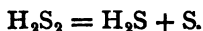
The solution so obtained is very freely employed as an analytical reagent for purposes that will be explained in Part III.

If sulphuretted hydrogen and water are chemical analogues, the question arises whether a body analogous to hydrogen peroxide (Experiment 78) may not be obtainable. In the case of the peroxide, we produced it by the action of an acid on barium peroxide; we shall now try to obtain the persulphide of hydrogen by an analogous method.

Experiment 287.—Mix equal weights of slaked lime and sulphur with about twenty times their weight of water; boil the mixture in an evaporating dish for some time, until a deep orange-coloured liquid is formed, then filter. Divide the filtrate into two parts; reserve one portion, and pour the other *slowly and with constant stirring into hydrochloric acid*, diluted with twice its volume of warm water, and contained

¹ This is a convenient test for the detection of *sulphides* in well waters or mineral springs.

in a conical glass. The mixture becomes milky, and a heavy oily liquid subsides and forms a layer at the bottom of the glass. Pour off the upper liquid and examine the oily body.¹ Note that when some of it is introduced into a test-tube along with a little water, and the mixture heated, sulphuretted hydrogen gas is evolved freely, and a residue of sulphur is left. This decomposition is evidently similar to that which occurs when hydrogen peroxide is heated (see Part I., page 139), and leads to the presumption that the yellow oil is the sulphur analogue of the peroxide, H_2S_2 , and that its decomposition by heat is represented by the equation—



As a matter of fact, however, the analysis of the body leads to the conclusion that it contains more sulphur than is indicated by the formula; but since the liquid is found to dissolve sulphur freely it is highly probable that the oily body is a solution of sulphur in the pure persulphide, and the source of this added sulphur is not far to seek.

When calcium hydrate and sulphur react in the proportions above given, soluble calcium sulphide, CaS_2 , is first formed, but the solution of disulphide easily dissolves more sulphur, forming more or less of higher sulphides of calcium, and these, on decomposition by acid, afford free sulphur as well as the persulphide.

Experiment 288.— Add slowly dilute hydrochloric acid to the orange liquid reserved from the last experi-

¹ This body may be kept for some time in presence of free hydrochloric acid, but is quickly decomposed by alkalis.

ment. Sulphuretted hydrogen gas is freely evolved, while a yellowish-white precipitate subsides, and soluble calcium chloride remains in solution. When the precipitate is collected, washed well with water and dried, it is found to possess all the characters of pure sulphur. This variety of sulphur is the *Lac sulphuris* or 'precipitated sulphur' (B.P.) Much of this variety of sulphur sold is adulterated with calcium sulphate, arising from the use of sulphuric instead of hydrochloric acid in the precipitation; the former affords nearly insoluble calcium sulphate, which is precipitated along with the sulphur. A sample of sulphur so mixed is easily detected by heating a small quantity on a slip of platinum foil; if the sulphur be pure it will wholly disappear, whereas, if adulterated, it will leave a considerable residue, which cannot be volatilised.

It will be noted that the same solutions are employed in Experiments 287 and 288. In the former the sulphur solution is added *to the acid*, which is therefore always in excess, and the persulphide is produced; in Experiment 288 the acid is slowly added *to excess of the alkaline sulphur solution*, and free sulphur is obtained, while sulphuretted hydrogen gas is evolved. The cause of this remarkable difference is due to the fact that the persulphide is decomposed by an alkaline liquid, and therefore cannot be formed in such a solution; hence sulphur and sulphuretted hydrogen appear in its stead.

Three chlorides of sulphur are known, viz., S_2Cl_2 , SCl_2 , and SCl_4 , as well as bromides and iodides; but the student may advantageously defer their study to a later stage of his course.

CHAPTER XXIII.

EXPERIMENTS WITH OXIDES AND ACIDS OF SULPHUR.

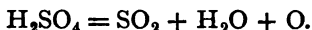
SULPHUR DIOXIDE = SO_2 . 1 Vol weighs 32 c.grs.
Molecular weight = 64.—Having thus reached elemental sulphur again after an examination of its hydrogen compounds, we shall now deal with the product of the union of the element with oxygen that we obtained in Experiment 272. From that experiment we learned that the product is gaseous, and that it possesses a very characteristic and suffocating odour.

When the experiment is conducted quantitatively, it has been found that every 32 c.grs. of sulphur burned in excess of oxygen produce 64 c.grs. of the oxide, and the specific gravity of this gaseous oxide is 32 ($\text{H} = 1$), or rather more than *twice* that of air; therefore its formula is SO_2 , and the molecular weight of the gas = 64.¹

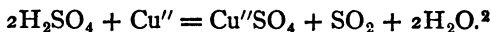
As the combustion of sulphur in oxygen or air is not a convenient source of the gas for experimental purposes, though very useful when we desire to diffuse a quantity of the dioxide through the air of a room as a powerful disinfectant, we must seek for another process for its preparation.

¹ Sulphur does not directly unite with more than two atoms of oxygen, save under special conditions, realised in Experiment 308.

Obviously sulphuric acid, H_2SO_4 , should afford the gas if we could remove from the acid an atom of oxygen and a molecule of water, thus—



Experiment 289.—Gently heat¹ together in a test-tube some strong oil of vitriol in which copper turnings are immersed. Soon bubbles of gas are evolved, and this gas has the unmistakable odour of sulphur dioxide. The following equation expresses this change—



In this case the atom of Cu displaces from one molecule of sulphuric acid its hydrogen, and the latter, at the moment of its liberation in the hot and strong liquid, acts upon another molecule of sulphuric acid and removes an atom of oxygen, forming therewith water, while the residue breaks up into sulphur dioxide and a second molecule of water.

Experiment 290.—Heat in a test-tube, as before, some strong oil of vitriol with a little coarsely powdered charcoal. Note that in this case also the smell of the dioxide is soon detected; but if a glass rod moistened with lime-water be held in the mouth of the tube,³ a white coating is soon produced, indicating the

¹ In heating sulphuric acid in a tube or flask great care must be taken lest the vessel should break and the hot corrosive liquid escape.

² Mercury may be substituted for copper in this experiment, when mercuric sulphate, HgSO_4 , is formed.

³ No drop of liquid should be allowed to fall into the tube containing the hot oil of vitriol, else dangerous spirting may take place.

presence of carbon dioxide as well as sulphur dioxide; the decomposition is correctly represented by the equation—



This mode of preparing sulphur dioxide is sometimes employed, and notably it is recommended in the British Pharmacopœia (under *Acidum sulphurosum*); but the presence of the carbon dioxide gas renders it inconvenient; hence we shall adopt the copper process.

Experiment 291.—Fit up a Florence flask with a delivery tube bent twice at right angles, and introduce about 20 grams of copper turnings; just cover these with strong oil of vitriol, and heat gently and carefully as already advised, having an earthen dish or plate under the whole apparatus in case of breakage of the flask. The gas is freely evolved, and, owing to its high specific gravity, it can be easily collected in jars by downward displacement of air. Collect in this way several jars of the gas; then withdraw the heat from the generating flask, and reserve the apparatus for further use. Note that the gas is colourless, has the suffocating smell already noticed, and that it does not burn when a lighted taper is lowered into it, but quickly extinguishes the flame.

Advantage is sometimes taken of the latter property for the purpose of extinguishing a 'chimney on fire,' or rather the burning soot within it. A handful of sulphur is thrown on the burning embers in the grate, and the sulphur dioxide arising from its combustion quickly checks the fire, especially if the air-supply to the chimney be limited as far as possible.

Experiment 292.—Pass the delivery tube of the apparatus into a tube of the form of fig 105, immersed in a mixture of ice and salt in equal parts. On applying gentle heat to the flask a slow current of the dioxide passes into the tube, and is thus cooled down below -10°C. , at which temperature it becomes a colourless liquid. When sufficient of the latter has been collected, withdraw the delivery tube, and, while retaining the vessel in the cooling mixture, apply a small flame to the contracted portion of the tube, then urge the flame with a blow-pipe until the glass softens and the narrow neck can be drawn out and its end hermetically sealed. When the end is quite cold, remove from the freezing mixture. The dioxide remains liquid at ordinary temperatures if thus sealed up in a moderately strong tube. The pressure exerted by the vapour is rather less than 2.5 atmospheres at ordinary temperatures. The liquefied oxide is now sold in siphons.

FIG. 105.



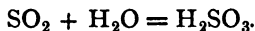
If the end be broken off a tube containing a little of the condensed dioxide, the liquid boils rapidly, and is soon converted into gas, but this change of state is accompanied by a great loss of heat, and if the tube from which the dioxide thus rapidly evaporates be moistened externally with water, the latter is quickly frozen; in this way a temperature as low as -50°C. can be reached, so that mercury can be easily solidified.

Experiment 293.—Shake up a jar full of the gas with some water. Note that considerable absorption takes place. Therefore the gas is easily soluble in

water. 1 c.c. of water can dissolve 43·5 c.cs. of the gas at 15° C.

Add to the liquid a few drops of litmus solution, and note that an *acid* is produced; the dioxide is therefore an acid-producing oxide, as we have already learned from Experiment 59.

Experiment 294.—The *Acidum sulphurosum* (B.P.) is a saturated aqueous solution of the gas, the latter being produced by heating oil of vitriol and charcoal, as in Experiment 290. Saturate some water with the gas obtained from copper and sulphuric acid; cool the saturated solution of the gas in water to zero by immersing the bottle in a mixture of ice and salt. Crystals separate which contain the body H_2SO_3 , or *sulphurous acid*, along with a somewhat variable proportion of water. This body is obviously the product of the union of sulphur dioxide, or sulphurous anhydride, with a molecule of water—



The acid is so unstable that it is decomposed completely on boiling, into the gaseous sulphur dioxide and water.

Experiment 295.—Pass sulphur dioxide into a solution of pure recrystallised sodium carbonate until no further effervescence is produced, and evaporate the solution until crystals begin to form; then set aside to cool. When the crystallisation is complete, drain away the mother-liquor and dry the crystals on blotting-paper. The composition of the salt is represented by the formula $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, though a compound with a larger proportion of water of

crystallisation is sometimes obtained when the solution is evaporated at low temperatures.¹

Experiment 296.—Warm the mother-liquor obtained in the last experiment, then saturate it completely with sulphur dioxide gas, and allow it to cool, when shining crystals of the sodium and hydrogen sulphite will separate— NaHSO_3 . Therefore sulphurous acid is dibasic.²

Experiment 297.—The salt produced in Experiment 295 has a somewhat alkaline taste and reaction, and is quite free from the smell of sulphur dioxide. Add a crystal to a few drops of strong (or dilute) oil of vitriol contained in a test-tube. Note that the dioxide is at once liberated, and may be easily recognised by its odour. All sulphites act in this way—



Experiment 298.—Add to a solution of the sulphite some solution of barium nitrate, $\text{Ba}''(\text{NO}_3)_2$, and note that a white precipitate is formed— $\text{Ba}'\text{SO}_3$ —which disappears almost completely³ on the addition of a few drops of hydrochloric acid, because the barium *sulphite* is soluble in the acid. Add now to the solution a few drops of chlorine water, and observe that a white precipitate appears; this new precipitate is found on analysis to consist of barium *sulphate*, BaSO_4 , which is not soluble in hydrochloric or other acid. In this

¹ For the use of sulphites as antichlores see page 247.

² On determination of basicity of acids see page 27, Part II.

³ If the liquid be quite fresh and the sulphite recently prepared, the precipitate disappears completely, but if partially oxidised to *sulphate* the solution is incomplete.

case, as in others we have already met with, chlorine evidently acts as an indirect oxidising agent, thus—



Experiment 299.—Add to some sulphurous acid a few drops of hydrochloric acid, followed by barium nitrate. No material precipitate is produced, but on addition of chlorine water the insoluble barium sulphate is formed as before, and hydrochloric acid as a by-product.

Experiment 300.—We already know that iodine acts as an indirect oxidising agent like chlorine (see Experiment 149); therefore add to a little sulphurous acid some aqueous solution of iodine in potassium iodide. The brown colour of the iodine quickly disappears, and if a *portion* of the liquid be poured into another tube and tested with barium nitrate and hydrochloric acid, an abundant precipitate of barium sulphate will appear; hence the action of iodine on the acid may be thus represented—



Now continue to add iodine solution to the portion of the liquid reserved until the latter becomes coloured by free iodine in excess; then dilute with a considerable volume of water, and note that the colour of the iodine disappears, and the liquid will decolourise a further quantity of iodine; in fact, the above reaction is only complete in very dilute solutions.

Experiment 301.—Dip a blush or red rose into sulphurous acid; the colour is apparently destroyed, but if the rose be removed quickly and plunged into

diluted sulphuric acid, the colour reappears, unless the action of the bleaching agent has been very prolonged.

Experiment 302.—Add a few drops of Condyl's fluid (potassium permanganate solution) to some water, and then sulphurous acid. The beautiful purple colour is destroyed, and cannot be restored, while the barium test proves that sulphuric acid has been formed, obviously at the expense of the highly oxidised permanganate (see Experiment 106, *b*).

Thus in certain cases sulphurous acid and the dioxide act as powerful *reducing* or deoxidising agents; where this change is accompanied by bleaching the latter is permanent. In other instances, as in that of the rose, it is doubtful whether the loss of colour is not wholly or in great part due to direct combination resulting in the production of a colourless body, which can again be made to afford the original tint by chemical treatment. Although a bleaching agent of moderate power, sulphur dioxide is used in cases where the employment of the more energetic chlorine would injure delicate tissues, as in the cases of silk and wool.

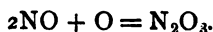
Sulphur dioxide, sulphurous acid, and sulphites are powerful *antiseptics*—that is to say, they arrest processes of fermentation, destroying the vitality of the organisms which are concerned in changes of the class referred to. Moreover, since low forms of life are destroyed by the dioxide, it is very often employed in the *disinfection* of rooms in which cases of infectious disease have been treated. For this purpose the apertures are carefully closed, and

quantity of sulphur dioxide is generated in the room by throwing sublimed sulphur on some red-hot coals contained in an iron vessel. After twenty-four hours the room may be opened, aired, and cleaned. Illustrations of the effects of sulphurous acid on fermentation will be met with in Part IV.

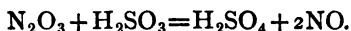
SULPHURIC ACID = H_2SO_4 . *Molecular weight* = 98.—The results of several of the experiments already made indicate very clearly that *sulphurous* acid quickly becomes *sulphuric* acid by union with an atom of oxygen derived from a compound of that element ; but sulphurous acid combines with *free* oxygen very slowly, for the solution may be exposed to the air for many days without losing its characteristic smell. We know already that nitric oxide gas affords a mixture of ruddy-coloured higher oxides of nitrogen on mere addition of atmospheric air ; we shall next try whether sulphurous acid can remove this added oxygen.

Experiment 303.—Fill a stoppered bottle with nitric oxide gas prepared as in Experiment 107 ; remove the stopper and allow air to mix with the colourless gas ; ruddy fumes are produced, consisting largely of N_2O_3 . Now pour into the bottle a few cubic centimeters of sulphurous acid solution, insert the stopper, and shake ; the gas is rapidly decolorised. Remove the stopper and admit air ; the ruddy colour of the gas reappears, and can be again removed by shaking with some more sulphurous acid ; and this set of changes can be repeated several times with the single charge of nitric oxide. Next test the liquid

for sulphuric acid with barium nitrate, followed by hydrochloric acid, and note that a strong precipitate of barium sulphate is formed ; therefore the sulphurous acid is changed to sulphuric acid. The explanation of the set of changes is obvious enough when viewed in the light of former experiments. The first stage is the formation of at least nitrogen trioxide—



Then the trioxide reacts with the sulphurous acid, thus—



The reproduced nitric oxide then takes a further supply of oxygen from the fresh air introduced, and passes it on to another quantity of sulphurous acid, and so on. There is therefore no theoretic limit to the oxidising action of the nitric acid, but practically the gas in time becomes so much diluted with the residual nitrogen of the air that the volume is inconveniently great. On the manufacturing scale advantage is taken of this important property of nitric oxide for the cheap production of oil of vitriol or sulphuric acid, and the chief changes that take place in the course of the manufacture are well illustrated by the simple experiment just described, the main points of difference being that the nitric oxide is directly derived from nitric acid, and that a mixture of sulphur dioxide gas and steam is used instead of sulphurous acid. The operation is conducted in a large leaden chamber, a simple form of which is shown in outline section, fig. 106. Steam, derived from a boiler *b*, is

blown into the chamber from the jets shown. The supply of sulphur dioxide is obtained by the combustion of iron pyrites— FeS_2 —in the furnace *f*, when—

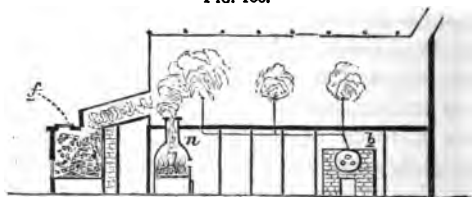


Nitric acid vapour enters from a small furnace *n*, in which is heated an iron pot containing sodium nitrate, or Chili nitre, and sufficient sulphuric acid to decompose it (see page 25, Part II.). The first reaction that we may assume to take place within the chamber is between nitric acid, sulphur dioxide, and water—



The nitric oxide thus produced combines with oxygen derived from the air within the chamber; higher

FIG. 106.



oxides of nitrogen are formed, only to be again quickly reduced to nitric oxide by more sulphur dioxide, an additional quantity of sulphuric acid resulting. A current of air and other gases is maintained through the chamber by a chimney with a powerful draught, but between the chamber and chimney is a tall 'Gay-Lussac's tower' containing coke, over which some

¹ The combustion of the pyrites once started is maintained without extraneous fuel, as sufficient heat is developed during the union of the sulphur and iron with the oxygen of the air.

strong oil of vitriol trickles; the waste gases are obliged to pass up through this tower, and are thus brought in contact with a large surface of sulphuric acid, which latter absorbs the oxides of nitrogen, and trickles from the tower charged with those bodies; this acid is then employed in the nitric acid furnace, where its nitrogen oxides are evolved and again become available.¹

The sulphuric acid formed in the above series of reactions collects along with some water on the floor of the chamber, and can be drawn off and tested. As soon as the specific gravity of the acid reaches from 1.5 to 1.6 (water=1), it is removed, and can be directly employed for many technical purposes; but in order to convert it into the 'oil of vitriol' of commerce it is heated in glass or platinum retorts until most of the diluting water has distilled off and only pure sulphuric acid begins to come over. This concentrated acid has a specific gravity of 1.84 when cold, and then appears as an oily liquid which distils at a temperature of 338° C. The ordinary oil of vitriol contains in solution oxides of nitrogen and arsenic derived from the pyrites. In order to free it from these it is distilled with ammonium chloride, and the first portions of the distillate (which contain arsenic chloride)

¹ In some works this strong nitrated acid is mixed with weak acid derived from the chamber, and the mixture trickles over flints contained in a 'Glover's tower,' which is interposed between the sulphur furnace and the chamber. On dilution with weak acid, the oxides of nitrogen are evolved from the liquid obtained in the Gay-Lussac tower, and are swept along into the leaden chamber by a current of hot sulphur dioxide, which at the same time concentrates the acid.

are rejected, and succeeding portions collected apart for use. The nitrous compounds decompose with the ammonium, and afford nitrogen gas and water. If in the course of manufacture the supply of steam to the sulphuric acid chamber be insufficient, white crystals are formed, whose composition is represented by the formula HSO_3NO_2 . These are termed 'chamber crystals,' and are easily decomposed by steam into sulphuric acid and oxide of nitrogen.

Experiment 304.—Mix very slowly and with frequent stirring four parts of strong oil of vitriol with one of water in a porcelain capsule; great heat is evolved, and a thermometer immersed in the mixture indicates a temperature of 140°C . or more, according to the strength of the acid used. If the product be cooled to 0°C . crystals separate whose composition is H_2SO_4 , H_2O ; the evolution of heat in the experiment is therefore due to the formation of a definite hydrate.

The avidity with which strong sulphuric acid seizes water renders it a valuable drying agent for gases, since it absorbs the aqueous vapour with which they may be mixed when the moist gases are made to bubble through the acid; and we have used it in Experiment 284 as a desiccating agent for a moist solid. We have already had illustrations of chemical changes that can be traced to its powerful dehydrating action, as in the decomposition of oxalic acid, Experiment 249, and of alcohol, Experiment 256. In some instances the abstraction of the elements of water from organic bodies leaves only carbon, and charring results from the action of the acid.

Experiment 305.—Dip a wooden match into some strong oil of vitriol and water ; note that blackening occurs. This is a convenient test for the strong acid.

Experiment 306.—Dilute some oil of vitriol by adding one part of the acid slowly and with frequent stirring to twelve of water ; the product is the *diluted sulphuric acid*¹ (B.P.) When cold use the liquid as ink for a quill pen, and write on paper. Hold the paper before a fire, and note that charring occurs as the ink dries, for the diluted acid loses water when heated, and the concentrated residue then acts on the tissue, which, like wood, consists of carbon, hydrogen, and oxygen. Similarly oil of vitriol added to a strong solution of white sugar causes the separation of a black solid which is nearly pure carbon.

Poisonous Action.—These observations leave no doubt that oil of vitriol is a highly *corrosive acid* ; hence it should be handled with care, as it can destroy the skin and other tissues, and has often caused serious accidents. Diluted sulphuric acid does not produce any injurious effects on the animal organism when taken in moderate doses, but the strong acid is a violent irritant poison, whose effects, like those of nitric acid, are due to its local corrosive action. The most suitable chemical antidotes are calcined mag-

¹ The impure acid, when diluted with water, often affords a turbid mixture ; this is due to the separation of white lead sulphate, $PbSO_4$, which is soluble in the strong acid, but insoluble in the diluted liquid. The lead compound is derived from leaden vessels in which the chamber acid is sometimes evaporated, or from the material of the chamber.

nesia diffused through water, or borax solution, followed by oily or mucilaginous drinks.

Experiment 307.—Test the diluted acid with barium nitrate, and note that the white precipitate of barium sulphate already obtained in Experiment 298 is formed, and that this precipitate is insoluble in dilute hydrochloric acid.

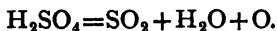
Hydrofluosilicic acid (see Experiment 209, *a*) also gives a precipitate with barium nitrate, which is insoluble in hydrochloric acid; but the two precipitates are easily distinguished by treatment described in 209, *c*, as barium sulphate is unacted upon by oil of vitriol, whereas the silicofluoride affords silicon tetrafluoride and hydrofluoric acid.

The barium test equally applies to the free acid and to metallic or other sulphates soluble in water, while the free acid is distinguished by its reaction to litmus-paper and corrosive effects when concentrated.

The ease with which sulphuric acid displaces more volatile or feebler acids from their compounds has been frequently illustrated in the course of our experiments—e.g., in the production of nitric and hydrochloric acids—and its great power in this respect renders it a most valuable chemical agent. In dealing with the preparation of nitric acid it was pointed out that two distinct classes of sulphates can be obtained, according as one or two molecules of potassium or sodium nitrate react with one molecule of sulphuric acid—viz., KHSO_4 and Na_2SO_4 , the analogue of K_2SO_4 . The formula of the acid deduced from its analysis cannot be represented by any lower

expression than H_2SO_4 ,¹ since the molecule cannot contain less than one atom of sulphur, and the hydrogen of the acid can, as we have seen, be replaced in two stages, affording an acid sulphate, KHSO_4 , and a neutral salt, K_2SO_4 , but no other than these two classes of compounds; therefore sulphuric acid is *di-basic*. A direct determination of the basicity of the acid can obviously be made by an analogous method to that described in the case of nitric acid.

We are already acquainted with the anhydride of sulphurous acid, SO_2 , and analogy would lead us to suspect the existence of a corresponding anhydride of sulphuric acid—that is to say, a body represented by the formula SO_3 . We know that sulphurous acid affords its anhydride on simple heating, but sulphuric acid distils without apparent change, and if strongly heated, as when it is dropped on red-hot platinum, it is decomposed, and affords sulphur dioxide, easily recognised by its smell, oxygen gas, and water, thus—



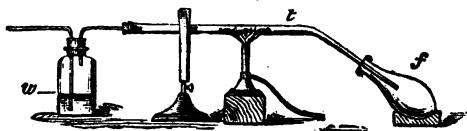
Moreover, we know that when sulphur burns in excess of air or oxygen it produces only SO_2 . If, however, we bring the dioxide and oxygen together under the following conditions, we can effect the desired union.

Experiment 308.—Make a current of oxygen gas, derived from a bag or gas-holder, bubble through strong sulphurous acid contained in the wash-bottle

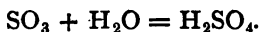
¹ The specific gravity of the vapour of sulphuric acid is only 25 ($\text{H} = 1$) instead of 45, the density required by the formula. This result is due to the decomposition of the acid at 440°C . into water and a trioxide of sulphur.

w, fig. 107, and then pass through the tube *t*, in which is heated some asbestos, coated with spongy platinum.¹ The oxygen carries along with it some sulphur dioxide gas derived from the solution, and their union takes place in presence of the hot finely-divided platinum, though the latter does not undergo any change that can be detected; dense white fumes issue from the tube, and can be condensed in the cold flask *f*. A white crystalline solid body is thus

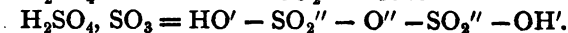
FIG. 107.



obtained, which is found on analysis to be sulphur trioxide, SO_3 , and to afford sulphuric acid when dissolved in water—



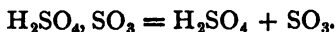
It is therefore sulphuric anhydride. This sulphur trioxide dissolves in oil of vitriol, and forms anhydrosulphuric acid, H_2SO_4 , SO_3 —a body whose relation to sulphuric acid is easily recognised if we write the formulæ thus—



¹ Moisten asbestos fibres with solution of platinum tetrachloride, PtCl_4 , dry and heat strongly in a porcelain crucible; the salt is completely decomposed, and finely divided platinum left on the asbestos, which latter thus platinised is to be used in the experiment.

The same body is obtained as a fuming acid liquid by heating dried and partially oxidised iron sulphate in clay retorts. The brown acid that distils over is termed *Nordhausen* acid, because originally prepared in the Saxon town of that name. Until recently this acid was much used by dyers for dissolving *indigo*, but the ordinary acid is now employed for this purpose.

When the Nordhausen acid is heated it gives off white fumes of sulphur trioxide, and considerable quantities of the latter can be thus conveniently obtained—



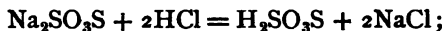
We know that sulphurous acid or sodium sulphite can unite with oxygen and form sulphuric acid or a sulphate; now sulphur and oxygen often play similar parts in chemical compounds, and the question arises whether a sulphite can unite with sulphur instead of oxygen.

Experiment 309.—Dissolve a small quantity of sodium sulphite, Na_2SO_3 , in some water contained in a test-tube; digest with it some sublimed sulphur for ten minutes at a gentle heat, then filter the solution. If the liquid be strong enough, crystals of a salt whose composition is $\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$ separate. This body may be regarded as sodium sulphate containing an atom of sulphur instead of one of the oxygen atoms, and is a *thio-sulphate*.¹

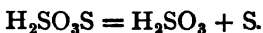
Sulphate	.	.	.	Na_2SO_4
Thio-sulphate	.	.	.	$\text{Na}_2\text{SO}_3\text{S}$

¹ *thio*, sulphur.

Add to a portion of the solution of the crystals some diluted hydrochloric acid. At first there is no apparent change, but presently the liquid becomes milky, and a smell of sulphur dioxide is perceived. Hydrochloric acid really liberates thio-sulphuric acid at first thus—

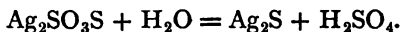


and the new acid, being very unstable, quickly decomposes thus—



A similar decomposition takes place when the crystals of the salt are heated with strong sulphuric acid in a test-tube, the separation of sulphur as well as evolution of sulphur dioxide serving to distinguish the salt from a sulphite, which only evolves SO_2 . Moreover barium nitrate only affords a precipitate in very strong solutions of the thio-sulphate and after shaking for some time; the precipitate dissolves in hydrochloric acid, but the liquid almost immediately decomposes as above.

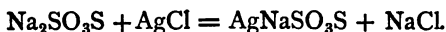
Experiment 310.—Add to a solution of the thio-sulphate a few drops of silver nitrate; a white precipitate is formed, which speedily blackens on heating the mixture, owing to the formation of silver sulphide, Ag_2S , and sulphuric acid, thus—



Experiment 311.—Add a little chlorine water to solution of the thio-sulphate. Note that the odour of the chlorine disappears, and the liquid does not

set free iodine from potassium iodide ; the thio-sulphate has therefore removed the free chlorine just as a sulphite or sulphurous acid can do. In the arts advantage is taken of this power in order to secure the removal of all traces of chlorine from bleached materials ; the tissue is soaked in a weak solution of a sulphite or thio-sulphate (and the latter is now preferably employed), which eliminate residual chlorine, and secure the material against slow disintegration by that body. These salts are technically termed 'anti-chlores.'

Experiment 312.—Prepare some silver chloride by addition of common salt (NaCl) to silver nitrate solution ; allow the precipitate of the chloride to settle, then pour off the liquid and replace by a strong solution of sodium thio-sulphate. Note that the silver chloride quickly dissolves, and the solution does not deposit silver sulphide for a considerable time. The solution depends upon the formation of a soluble and tolerably permanent thio-sulphate of sodium and silver, thus—

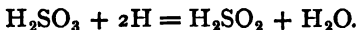


This property of the thio-sulphate is of great importance in photographic processes, as a strong solution of the salt is employed for the removal of chloride or other insoluble silver salt that remains unchanged on a print or collodion film after the action of light. This solution of the silver salts unacted upon by light is essential to the permanence of the image formed by their decomposition under the influence of the solar

rays; therefore this process of removal is termed 'fixing.'

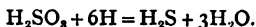
The salt which presents the properties just determined is commonly termed 'hyposulphite of soda,' and is so named in the 1867 edition of the 'British Pharmacopœia.' This name is, however, incorrect, as the reactions of the body, above pointed out, leave no doubt that it is a sulphur-sulphate; moreover the true hyposulphite is known and is easily formed in the following manner.

Experiment 313.—Introduce some sulphurous acid into a well-stoppered bottle containing clean strips of zinc, insert the stopper, and allow the whole to stand for some time. The zinc displaces hydrogen, but the latter is not evolved as gas, for it reduces the sulphurous acid to hyposulphurous,¹ thus—



The brownish solution obtained absorbs oxygen with avidity even from atmospheric air; hence it is a powerful reducing agent, and a few drops added to silver nitrate quickly reduces the metal; moreover, when solution of indigo is dropped into another portion of the liquid the blue colour disappears.

¹ If a very small proportion of sulphurous acid be added to a liquid in which hydrogen is rapidly generated by the action of zinc on hydrochloric acid, the reduction proceeds further, and sulphuretted hydrogen is produced—



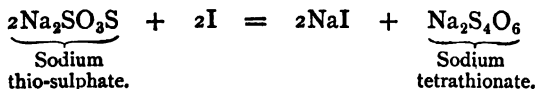
The sulphuretted hydrogen can be easily detected by its smell and its action on lead-paper.

We have thus recognised the following group of sulphur acids :—

Hydrosulphuric acid (sulphuretted hydrogen)	. H ₂ S
Hyposulphurous acid H ₂ SO ₂
Sulphurous acid H ₂ SO ₃
Sulphuric acid H ₂ SO ₄
Thio-sulphuric acid H ₂ SO ₃ S

The sodium salt of the last-named acid—sodium thio-sulphate—is readily converted by means of iodine into the corresponding salt of a complex acid belonging to a distinct series.

Experiment 314.—Add solution of iodine in potassium iodide to solution of thio-sulphate until the yellow colour of the iodine ceases to disappear; the solution then affords on crystallisation the salt referred to, which is thus formed, along with sodium iodide—



This product is derived from the acid H₂S₄O₆, which is the third known member of the following series of sulphur acids—often termed the *thionic series*, in order to distinguish them from the preceding :—

Dithionic acid H ₂ S ₂ O ₆
Trithionic acid H ₂ S ₃ O ₆
Tetrathionic acid H ₂ S ₄ O ₆
Pentathionic acid H ₂ S ₅ O ₆

These bodies are not yet of sufficient importance to demand further notice in an elementary course.

There can be no doubt that sulphur is at least a four-link or tetratomic element in its higher acids, but many chemists consider it to act as a hexad in sulphuric acid and anhydride.

Closely related to sulphur are the two rare elements SELENIUM and TELLURIUM. The former is found in combination, chiefly as lead selenide—the analogue of lead sulphide or galena ; and the latter to a small extent in the free state, but usually united with gold, silver, lead, and bismuth, as tellurides. Both elements form hydrogen compounds analogous to sulphuretted hydrogen, and several oxides and acids similar in composition to those obtained from sulphur ; hence sulphur, selenium, and tellurium form a small natural group, whose members, moreover, exhibit a distinct gradation in characters analogous to that traced in the group of halogens. Selenium occupies a position between sulphur and tellurium, and its atomic weight, =79, is nearly the mean of those of the other two elements, thus—

$$\begin{array}{rcl}
 \text{Sulphur} & = & 32 \\
 \text{Tellurium} & = & 128 \\
 & & \hline
 & & 160 \div 2 = 80.
 \end{array}$$

CHAPTER XXIV.

EXPERIMENTS WITH BORON COMPOUNDS.

BORON, B = 11.

Experiment 315.—Dissolve about 20 grams of common borax in 100 c.cs. of hot water, and add to the liquid 20 c.cs. of sulphuric acid, previously diluted with twice its volume of water. Note that crystals separate on cooling and can be easily collected on a filter, washed with a little cold water in order to free them from adherent sulphuric acid, and then air-dried. This compound, when quite pure, has the composition represented by the formula H_3BO_3 , and is termed *boracic acid*.

Experiment 316.—Dissolve some of the crystals in spirit of wine contained in a porcelain basin, and set fire to the spirit. Note that the flame is coloured *green*. This is characteristic of the acid.

Experiment 317.—Dip into the aqueous solution of some of the crystals a strip of yellow *turmeric*-paper; then dry the paper over a lamp, and note that the colour changes to *brownish-red*, and this tint is altered to dark blue or greenish-black when moistened with ammonium hydrate.

Experiment 318.—Heat some of the crystals in a

porcelain crucible, and note that they evidently lose water and ultimately fuse to a glassy mass. While heating, bring the flame of the lamp up to the edge of the crucible, and note that a strong green tint is communicated to the gas ; therefore the boracic acid is vaporised along with the current of steam ; but when all moisture has been driven off, the flame tint is very slight or imperceptible because it is only in presence of aqueous vapour that the body is volatile. The first effect of heat is to drive off a molecule of water and leave *metaboric acid*, HBO_2 —



Long-continued heating decomposes metaboric acid, and boric anhydride or boron sesquioxide— B_2O_3 —is left as a fused mass—

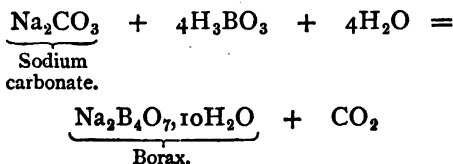


Experiment 319.—Powder some of the cleanest fragments of boric anhydride, and cover with the powder a small pellet of clean metallic sodium contained in a tube of hard glass. Heat the mixture strongly, then allow the tube to cool, break it and scrape out the contents, which should then be thrown into water. The latter dissolves out sodium oxide, and leaves a grey or greenish powder which is caught on a filter, washed with a little water, and dried. This powder is the element *boron*, $\text{B} = 11$. The element is slightly soluble in water. It is not volatile, and becomes liquid only at an intense white heat. When air is admitted to it at a high temperature it burns and re-forms the oxide ; if nitrogen only has access to it, a nitride of boron is directly formed. Several varieties

of boron have been obtained, but their elementary character is very doubtful.

One of the chief compounds of boron is the tri-basic boracic acid, H_3BO_3 . This acid is met with in the hot gases and vapours that issue from the earth in volcanic districts, but more especially in Tuscany. Rough basins (lagoons, or *lagoni* = little lakes) are built up round the mouths of the jets; these contain much water, through which the gases bubble, and in passing leave the boracic acid. The weak solutions thus obtained are concentrated by evaporation, which is effected with the aid of the natural heat of the gases, and the strong liquid when cooled deposits crystals of the crude acid, several thousand tons of which are annually exported from the district. Much of this is employed in the manufacture of borax.

Experiment 320.—Dissolve 10 grams of boracic acid and 12 grams of crystallised sodium carbonate in 30 c.cs. of hot water. Effervescence ensues, owing to the escape of carbon dioxide gas. When solution is complete, allow the liquid to cool and slowly evaporate as well, when colourless crystals are deposited. These are crystals of borax, thus formed—



This peculiar body is generally regarded as a compound of sodium metaborate with the anhydride, thus—

$(\text{Na}'\text{BO}_2)'_2\text{B}_2\text{O}_3, 10\text{H}_2\text{O}$. It is used to a small extent in medicine as a local application, chiefly to the mouth and throat, and as an antiseptic.

Experiment 321.—Make a small loop of thin platinum wire, moisten it with water, and dip it into some powdered borax. Much of the powder will adhere, and when the salt is introduced into the Bunsen gas-flame it is seen to swell up, owing to the escape of its water of crystallisation; on continuing the heat, the residue fuses, and a clear liquid is obtained, which, when removed from the flame, becomes a solid glassy bead. Now dip this bead in a solution of cobalt nitrate and fuse again; the bead is coloured a beautiful blue. This is due to the power of the molten borax to dissolve various metallic oxides, and form glasses of more or less characteristic tints; hence fused borax is a most useful blowpipe test for the following metals, whose compounds, when heated with it as above or in the outer blowpipe flame, afford the coloured beads noted:—

Cobalt	.	.	.	Blue
Copper	.	.	.	Pale blue or greenish
Iron	.	.	.	Reddish
Nickel	.	.	.	Red
Manganese	.	.	.	Violet
Chromium	.	.	.	Green

In consequence of this important power of dissolving oxides, borax is much used in the arts in soldering metals at high temperatures; the fused borax cleans the surfaces from oxides that would prevent the attachment of solder, and thus permits the desired union to be effected under a protecting varnish.

Experiment 322.—Dissolve some of the borax in water and note that it has a strong *alkaline* reaction to test-papers. When acidulated with hydrochloric acid, its solution can be tested with turmeric-paper as in Experiment 317, and the flame test applied by mixing with spirit and igniting the alcohol.

Experiment 323.—Take a fresh solution of borax, add barium nitrate to it, and note that a white precipitate of barium metaborate is formed, which is soluble in dilute hydrochloric acid.

Experiment 324.—Add silver nitrate to a fresh solution of the salt, and note that a dirty white or brownish-white precipitate is formed, which contains silver metaborate.

Boron forms a gaseous compound with hydrogen, whose formula has not yet been clearly determined by its discoverers, Messrs. Jones and Taylor, but which will probably prove to be BH_3 . It also forms a gaseous trifluoride which is decomposed by water in a similar manner to silicon tetrafluoride, and affords hydrofluoboric acid— HBF_4 —allied to the silicon acid. The element also forms a trichloride, $B'''Cl_3$. In all the gaseous or vaporous molecules of these bodies, the lowest weight of boron found is 11 units, hence 11 is the atomic weight of boron. The element is at least a triad, though resembling tetrad silicon and carbon in some respects, amongst others in having a heat capacity sensibly lower than that required by Dulong and Petit's law,¹ and in forming acids which are very weak at low temperatures and therefore easily

¹ The weight of boron that contains the same quantity of heat at 100° C. as 108 c.grs. of silver is 13 c.grs. instead of 11.

separated from their salts by comparatively feeble agents—in fact, the alkalinity of solution of borax is nearly as marked as that of caustic soda containing the same weight of alkali. An oxychloride of boron has, however, been recently obtained, and if the formula assigned to it— BOCl_3 —be established we must regard boron as a *pentad*, and related to a natural group that includes nitrogen and the interesting and important element phosphorus, whose compounds we shall next study.

CHAPTER XXV.

EXPERIMENTS WITH PHOSPHORUS AND ITS
COMPOUNDS.

PHOSPHORUS, $P^v=31$. *Weight of Gaseous Molecule = 124*.—We have already used the element phosphorus in several experiments, and since it is easily purchased we may at once proceed to determine its characters. As commonly sold, phosphorus is a yellowish, translucent, waxy solid, which is preserved in water, owing to the ease with which it ignites in air.

Experiment 325.—Obtain a stick of phosphorus, and cut a very small piece off *under water*; ¹ it cuts as easily as hard wax. Dry the fragment by gentle pressure between folds of bibulous paper, then place it on a piece of wood and rub with an earthen pestle; the phosphorus takes fire, burns vigorously, and soon inflames the wood; therefore phosphorus is easily ignited by friction.

The common form of match is tipped with a composition that contains free phosphorus, which latter ignites when the match-head is rubbed on sand-paper

¹ Too great care cannot be taken in handling waxy phosphorus, as it produces one of the most violent and persistent burns if inflamed in contact with the skin. Whenever possible it should be handled under water, in which it is perfectly safe.

attached to the side of the box. The modern 'safety matches' are prepared in a different manner, that will be described under Experiment 332.

Experiment 326.—Bring a stick of nearly dry phosphorus into a dark room, and observe that it is self-luminous,¹ emitting a pale greenish-yellow light, while luminous vapour is seen to be given off. This vapour has a strong and characteristic odour, resembling garlic.

If the element be enclosed in *pure* hydrogen or nitrogen gases, it is no longer luminous, but the addition of a small quantity of oxygen restores the luminosity, which is presumably due to slow oxidation. It is non-luminous in pure oxygen at ordinary pressure, but emits a very bright light when the gas is rarefied. The presence of sulphuretted hydrogen, ether, and turpentine vapours, &c., prevent the emission of light even in presence of oxygen.

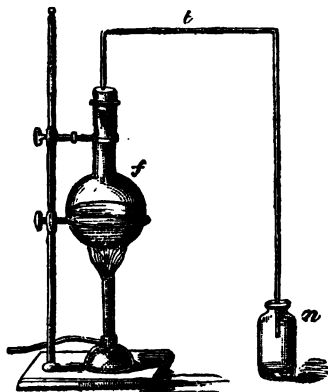
Experiment 327.—Add a piece of phosphorus about the size of a duck-shot to about five cubic centimeters of carbon disulphide. Note that the phosphorus dissolves very rapidly in the liquid, and the solubility of the element is so great that one part of the liquid can dissolve *eighteen* parts of phosphorus. Pour a few drops of the liquid on a small piece of *gun-cotton* placed on a plate; after a time the volatile disulphide evaporates, and leaves phosphorus behind in such a fine state of division that oxidation rapidly takes place, and the heat fires the gun-cotton, which disappears with a flash. The solution used is the

¹ The name of the element is derived from φωs, light, and φέρω, I bear.

dangerous liquid often termed 'Greek fire' or 'Fenian fire.'

Waxy phosphorus is very slightly soluble in water and alcohol, but is dissolved by ether, turpentine, resins, oils, fats, and wax. Its solution in animal fat, mixed with flour, sugar, and a little Prussian blue, constitutes the well-known 'phosphorus paste' which is freely used to destroy rats, and has often caused

FIG. 108.



the loss of human life, for the free element and its vapour are alike highly poisonous to animals.

A solution of phosphorus in balsam of Tolu and yellow wax is ordered in the British Pharmacopœia for the preparation of phosphorus pills, as minute doses of the free element are often medicinally administered.

Experiment 328.—The luminosity of phosphorus

affords an easy means of detection when the *free* element is present in a mixture. Arrange the apparatus shown in fig. 108, which consists of a flask *f*, and long condensing tube *b*, which latter dips into *n*. Introduce into *f* a little 'phosphorus paste,' and about half fill the flask with water, insert the cork, and apply heat. When the experiment is made in a dark room, the vapour over the contents of the flask is seen to be luminous, and when the liquid boils a bright flickering light traverses the tube, and by alternate cooling and heating of *f* the luminosity can be made to move backward and forward through the tube; then, on boiling steadily for some time, the vapour of phosphorus is carried over with the steam, and the contents of *n* occasionally become luminous, while minute globules of condensed phosphorus can often be obtained on the sides of the tube and in the bottle *n*.

This mode of detecting phosphorus was devised by Mitscherlich, and is named after him; it is the method always employed in testing the contents of a stomach, &c., for the poisonous element.

Experiment 329.—Place a small piece of waxy phosphorus in water contained in a flask, and gently heat. Note that when the temperature of the water reaches 45°C . the phosphorus melts, and in this state is a yellowish liquid of specific gravity 1.76. While in this condition it can be drawn into cylindrical moulds, in which it solidifies on cooling, and the sticks commonly sold are cast in this way. When liquid phosphorus is heated out of contact with the air, it is found to boil at a temperature of 290°C ., and the specific gravity of its vapour, even at temperatures far

beyond its boiling point, is 61.9 ($H = 1$); therefore its molecular weight is almost 124. Consequently the atomic weight of phosphorus should be 62; but we shall presently find that the highest atomic weight that can be assigned to the element on grounds similar to those stated in the cases of silicon, carbon, and boron, is 31. Now 31 is contained four times in 124; therefore the gaseous molecule of phosphorus contains *four* atoms, even at temperatures far above the boiling point of the element.¹

When waxy phosphorus is heated to 240° C. in a flask² or other vessel filled with nitrogen or carbon dioxide, a dark reddish solid is obtained after some hours, and if the heating be prolonged, the whole of the phosphorus undergoes this change, and a mass is obtained which does *not* dissolve in carbon disulphide, or it yields up only a small proportion of unchanged waxy phosphorus to the liquid. When all the ordinary variety of the element has been removed by the solvent, the friable residue is ground with water, then caught on a filter and dried; the specific gravity of this solid is 2.1. This is the *red* or *amorphous phosphorus*—a body which is prepared as described on the large scale, and, being an article of commerce, can be easily purchased. It need not be preserved under water, and bears moderate friction without ignition.

Experiment 330.—Float two small capsules on

¹ See under SULPHUR, p. 211.

² It is not advisable for a junior student to make amorphous phosphorus, as its preparation is attended with risk of serious burns, but it is desirable that he should obtain a small specimen for examination.

some water heated in a large porcelain or other dish, place in one a small quantity of the red phosphorus, and in the other a piece of the waxy variety. Note that the latter soon takes fire, while the former, if pure, may be heated for an indefinite time to the temperature of boiling water without igniting; if, however, it be touched with a wire heated to dull redness it burns violently, and affords white fumes in abundance, like the ordinary phosphorus. These fumes alike consist of the pentoxide, P_2O_5 , and equal weights of the two forms of the element afford equal weights of pentoxide; hence red phosphorus is but an allotropic modification of the element, just as diamond and graphite are of carbon. This remarkable body was discovered by Schrötter in 1845. Other varieties of phosphorus are known, but are not of any practical importance.

Experiment 331.—Introduce a little red phosphorus into a small glass tube closed at one end, and heat. When the temperature reaches 260° C., the waxy variety is suddenly reproduced, with much evolution of heat, and phosphorus vapour is evolved. Thus we can change at will one variety into the other.

Experiment 332.—Bring some red phosphorus into a dark room, and note that it does not emit luminous vapour (unless impure, owing to the presence of some of the waxy variety), nor is the solid phosphorescent.

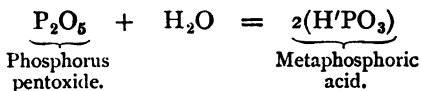
The non-volatility of red phosphorus is of great practical importance in the match manufacture, as the workpeople engaged in the industry when ordinary

waxy phosphorus was exclusively employed suffered from a most painful and fatal disease of the lower jaw, caused by the inhalation of small quantities of the poisonous vapour. Since Schrötter's valuable discovery the mortality arising from the cause referred to has been greatly reduced, as the red variety may be handled with impunity ; consequently its use in match-making is rapidly extending.

The 'safety matches' already mentioned are thus prepared. The wooden splints are tipped with a composition made up of glue, potassium chlorate, and antimony sulphide, with either red lead or the peroxide of the metal. When dry this match can be ignited by rubbing the composition it carries on a surface coated with a mixture of red phosphorus and fine sand ; a piece of paper so coated is usually attached to the side of the 'safety match-box,' hence the match does not carry the phosphorus, and the risk of accidental ignition is thus reduced to a minimum.

Experiment 333.—Place a small crucible containing a piece of dry waxy phosphorus on an ordinary earthenware plate ; kindle the phosphorus by touching with a hot wire, and invert over it a dry bell-jar. White fumes are produced in abundance, and partially settle on the sides of the jar and in part on the plate ; when the combustion is at an end allow a little time for the subsidence of the white substance, and it may then be rapidly collected and preserved in a stoppered bottle. Note that any of the white body exposed to the air quickly deliquesces, and produces a liquid which is highly *acid* to test-paper. The composition of the

white body is represented by the formula P_2O_5 ,¹ and this, when added to cold water or allowed to absorb moisture from the air, affords metaphosphoric acid, thus—



Experiment 334.—Test a few drops of the acid liquid thus obtained with ammonio-nitrate of silver,² and note that a *white* precipitate (of silver metaphosphate, $Ag'PO_3$) is obtained, which is very easily soluble in excess of the reagent or of acid.

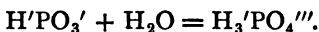
Experiment 335.—To another portion of the solution obtained in Experiment 333 add some diluted *white of egg*. Note that a white clotted material, *coagulated albumen*, forms.

Experiment 336.—Boil some of the metaphosphoric acid solution for some time, and then test a portion with the silver solution, when a *yellow* precipitate is obtained, while another portion is found to have lost the power of coagulating white of egg. The yellow silver compound is known to have the composition Ag_3PO_4 , and is evidently derived from a tribasic acid, H_3PO_4 , termed *ortho-phosphoric acid*, that results

¹ When the supply of oxygen to burning phosphorus is limited, the lower oxide P_2O_3 is produced; this body unites with water, and produces *phosphorous acid*, H_3PO_3 (see also Experiment 170). Corresponding sulphides of phosphorus are known, but their preparation is attended with much danger.

² Obtained by adding NH_4OH to solution of $AgNO_3$, until the precipitate first formed is *just* redissolved.

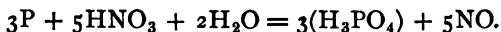
from the assumption of a molecule of water by meta-phosphoric acid—



These two acids are thus easily distinguished by their action with ammonio-nitrate of silver and white of egg.

A dilute solution of ortho-phosphoric is employed in medicine, and is prepared by the action of nitric acid on phosphorus, according to the directions of the British Pharmacopœia, thus :—

Experiment 337.—Introduce a fragment of phosphorus into a large test-tube, add some nitric acid previously diluted with its own volume of water, and heat gently. The phosphorus gradually dissolves on slow digestion, and nitric oxide gas is evolved, which produces brown fumes at the mouth of the tube. In this case—



Pour the liquid into an evaporating dish, and heat until all nitric acid fumes cease to be evolved, and a syrupy liquid remains. Dilute a little of this with water, and test it as above for ortho-phosphoric acid.

Experiment 338.—Evaporate the residue of last experiment in a porcelain crucible until water ceases to be evolved, and heat to redness for some time, then allow to cool. The interior of the vessel is seen to be coated with a glassy substance, which in large quantities has an *ice*-like appearance, and hence is termed *glacial* phosphoric acid. When this is dissolved in water it is found to possess the characters of meta-

phosphoric acid ; thus the ortho acid, when heated to redness for some time, loses the elements of water, and affords the metaphosphoric acid—

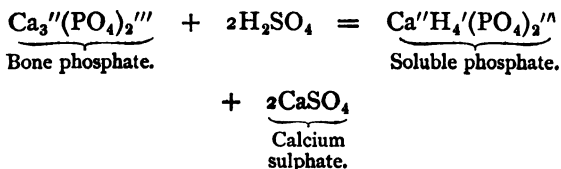


We shall presently find that there is an intermediate compound between the two acids, named *pyro-phosphoric acid*.

The common source of phosphorus and its compounds is calcium ortho-phosphate, $\text{Ca}_3''(\text{PO}_4)_2'''$, in a more or less impure condition. Bone-ash consists almost wholly of this phosphate (which is therefore the mineral base of bony tissue), and includes a small proportion of magnesium phosphate, calcium fluoride, and carbonate. The mineral *apatite* is a calcium phosphate containing a little fluoride and chloride; *coprolites* are also rich in calcium phosphates; and *guano*—the partially decomposed excreta of sea birds—owes much of its value to the large proportion of calcium phosphate which it contains.

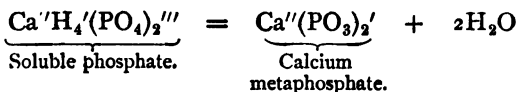
Experiment 339.—Powder about 20 grams of bone-ash, place it in a porcelain capsule, and pour upon it about 15 c.cs. of strong oil of vitriol, and mix well, gradually adding 30 c.cs. of water. Allow the mixture to stand for some days, taking care to stir occasionally ; then add about 100 c.cs. of water, boil for some time, and filter when cold. Note that the liquid which passes through the filter is strongly acid, but when a portion is tested with barium nitrate for sulphuric acid, it give a comparatively small precipitate undissolved by hydrochloric acid. The acid solution, when neutralised by ammonium hydrate,

gives a white precipitate consisting of a calcium phosphate¹—in fact, the acid solution obtained by treating bone-ash with sulphuric acid contains a soluble and acid calcium phosphate, $\text{Ca}''\text{H}_4'(\text{PO}_4)_2'''$. This compound is thus formed from the ordinary or insoluble phosphate—



When the liquid is filtered the nearly insoluble calcium sulphate is left, and the acid phosphate obtained in tolerably pure solution.

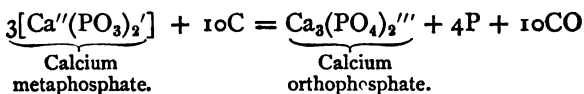
Manufacture of Phosphorus.—The production of the soluble phosphate is the first step in the process of manufacture of phosphorus from bone-ash; the succeeding stages are the following:—The solution obtained as above is evaporated nearly to dryness, the syrupy liquid mixed with charcoal, and the mixture strongly heated; the immediate effect of this treatment is the conversion of the acid orthophosphate into calcium metaphosphate—



The residue is then heated nearly to whiteness in earthen retorts; phosphorus distils over, and carbon

¹ $\text{Ca}''\text{HPO}_4$.

monoxide gas escapes, while a residue of calcium orthophosphate is left—



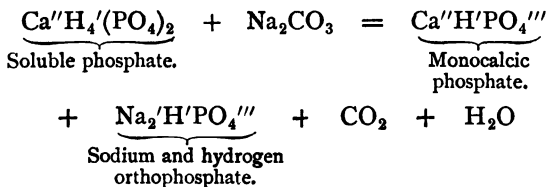
The phosphorus is condensed in water, and when in a molten condition is squeezed through thin leather to free it from impurity, and then cast into sticks.

Manufacture of 'Superphosphate of Lime' Manure.

The treatment carried out in our experiment with bone-ash is almost exactly that employed in the preparation of this well-known manure on the large scale. The phosphatic material, whether bones, coprolites, or guano, is mixed by powerful machinery with chamber oil of vitriol, and the pasty mass transferred to pits or 'dens' capable of containing several hundred tons; here it undergoes the change represented by the equation, and when as nearly complete as possible the mass, which has now become friable, is broken up and sent into the market. This is used for increasing the fertility of the soil, since all crops require more or less phosphate for their healthy and vigorous development, and when the necessary supply is presented in an easily soluble form it is immediately available as plant food, since the roots can only absorb mineral matter when the latter is presented in solution.

Experiment 340.—Add solution of sodium carbonate to the acid phosphate prepared in the last experiment, and note that a white precipitate is formed and CO_2 gas is evolved; heat the mixture, and con-

tinue the addition of the carbonate until the liquid acquires a distinct alkaline reaction ; then filter. The precipitate caught on the filter is a monocalcic phosphate— CaHPO_4 —thus produced—



Evaporate the clear liquid until crystals form, when the common sodium phosphate separates in hydrated form, as the crystals contain $\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$. This salt is the *phosphate of soda* of the British Pharmacopœia, whose directions we have substantially followed in its preparation. The compound loses some of its water of crystallisation when exposed to dry air, and is then said to *effloresce*. Note that the solution of the salt is *alkaline* to test-paper, though the compound still contains hydrogen replaceable by a metal. By the addition of the requisite quantity (one molecule) of caustic soda to the above salt, trisodic phosphate— Na_3PO_4 —is obtained which has a strongly alkaline reaction.

Experiment 341.—Dissolve 18 grams of the common sodium phosphate in a small quantity of hot water, and add 3 grams of ammonium chloride previously dissolved in very little water. On cooling, crystals of the compound $\text{Na}'\text{NH}_4'\text{H}'\text{PO}_4, 4\text{H}_2\text{O}$ separate out, and sodium chloride remains in solution. This phosphate is termed *microcosmic salt*,

and is a good illustration of a tribasic acid in which all three basic radicles are different. This body is sometimes used in blowpipe testing, for when heated strongly it leaves only sodium metaphosphate, NaPO_3 , and this salt, like borax, when fused with certain metallic oxides, dissolves them, and affords characteristically coloured beads.

Experiment 342.—Heat a crystal or two of sodium or other phosphate in a test-tube with a few drops of oil of vitriol. No gas or vapour is given off, as phosphoric acid is not volatile.

Experiment 343.—To a solution of the sodium salt add barium nitrate; a precipitate of barium phosphate, $\text{Ba}_3''(\text{PO}_4)_2'''$, forms, which readily dissolves in hydrochloric acid.

Experiment 344.—Solution of silver nitrate gives a yellow precipitate of $\text{Ag}_3'\text{PO}_4'''$ in a solution of an orthophosphate.¹

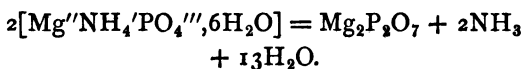
Experiment 345.—Solution of magnesium sulphate, followed by ammonium hydrate, affords a precipitate with a solution of alkaline orthophosphate. If the solutions are dilute, the precipitate falls slowly, assuming a crystalline condition, and if the liquid be stirred with a glass rod crystals form along the lines of contact of the rod and the sides of the tube. The body deposited has the composition—



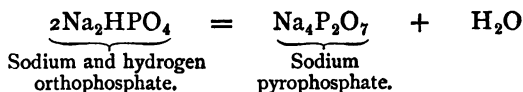
¹ Another excellent but expensive test is *ammonium molybdate*, whose solution affords with an orthophosphate, on gently warming, a yellow precipitate insoluble in nitric acid. This precipitate contains a phosphomolybdic acid of complex composition.

Formation of Sodium Pyrophosphate. 271

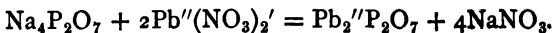
and is sometimes termed *triple phosphate*, more especially when met with as a urinary deposit. When this compound is heated strongly in a tube or crucible, water and ammonia gas are given off, and the residue has the composition $\text{Mg}_2''\text{P}_2\text{O}_7$, or *magnesium pyrophosphate*—



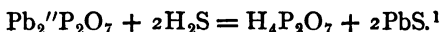
Experiment 346.—Heat in a crucible a few crystals of ordinary sodium phosphate. Note that the salt at first melts, and evolves much water, and if gentle heat be continued, a white residue is obtained which gives the usual *yellow* precipitate with silver nitrate when a portion is removed and tested; hence the heat has merely driven off the water of crystallisation without otherwise altering the salt. Now heat the residue in the crucible to redness for some time, and allow it to cool. When tested as before, its solution now gives a *white* precipitate with silver nitrate, and the body left by the ignition has the composition $\text{Na}_4'\text{P}_2\text{O}_7$, or that of *sodium pyrophosphate*, allied to the magnesium salt already obtained—



If the pyrophosphate be dissolved in water and solution of lead nitrate added, lead pyrophosphate is thrown down—

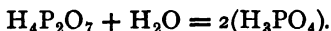


The lead compound can be caught on a filter, washed with water, and then, while moist, if it be scraped off the filter, diffused through some pure water, and a current of sulphuretted hydrogen gas passed through the mixture; insoluble and black-coloured lead sulphide is formed, and pyrophosphoric acid remains in solution; if the liquid then smells of sulphuretted hydrogen it should be shaken up with some more lead pyrophosphate until the odour disappears, and filtered—

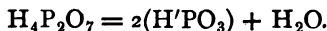


The acid solution, unlike metaphosphoric acid, does not coagulate albumen; and, unlike orthophosphoric acid, gives a *white* precipitate with ammonio-silver nitrate.

When the aqueous solution of pyrophosphoric acid is boiled for some time it is completely changed to orthophosphoric acid—



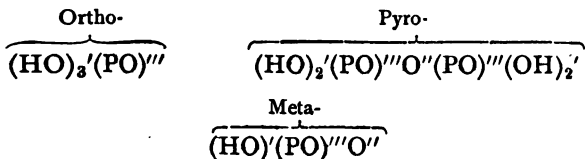
But if evaporated down at a low temperature and the residue then ignited, it is changed to metaphosphoric acid—



Pyrophosphoric acid is therefore a tetrabasic acid, intermediate between ortho- and metaphosphoric acids.

¹ The method here adopted is very frequently employed when we desire to obtain a free acid from its insoluble lead compound.

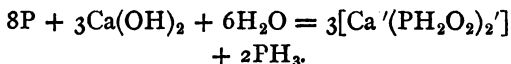
The constitutional formulæ of the three acids may be thus expressed, if we represent each to contain the triad group PO''' —



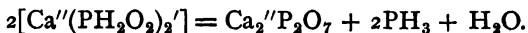
The existence of another tribasic acid of phosphorus has already been pointed out (page 254, note)—viz., phosphorous acid, H_3PO_3 —but it is not of sufficient importance to demand examination in this Elementary Course.

Experiment 347.—Add to some water in a test-tube half a gram or so of fresh slaked lime, $\text{Ca}''(\text{OH})_2'$, then drop in a fragment of phosphorus, and heat to boiling. Note that a peculiar smell is evolved as the phosphorus dissolves, and occasional bubbles of gas that rise through the liquid take fire spontaneously when they meet with air; this gas is found to be a gaseous compound of phosphorus with hydrogen—termed phosphuretted hydrogen—whose composition is PH_3 . When the phosphorus has dissolved, throw the liquid on a filter in order to separate undissolved calcium hydrate; evaporate almost to dryness the clear liquid that passes through, when a white crystalline residue is obtained which has a pearly lustre and a nauseous taste. This body is termed calcium hypophosphite, and is the 'hypophosphite of lime' of the British Pharmacopœia. Its formula

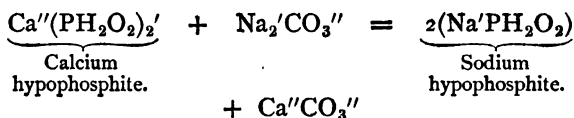
is $\text{Ca}''(\text{PH}_2\text{O}_2)_2'$, and it is the product of the following reaction—



If the calcium hypophosphite be dried and then heated in a small tube, it affords a quantity of the spontaneously inflammable phosphuretted hydrogen gas, and leaves calcium pyrophosphate, thus—



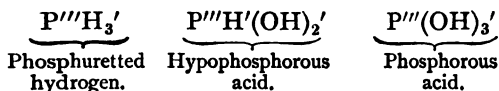
The sodium salt is easily prepared from that of calcium by precipitating the solution of the latter with sodium carbonate, filtering off the chalk thrown down, and evaporating the solution to dryness—



This is the process given in the B.P. for the preparation of the sodium salt; the latter, like that of calcium, is used in medicine, but the sodium hypophosphite may also be obtained by dissolving phosphorus in caustic soda, as in the next experiment. These metallic hypophosphites are easily distinguished by their property of affording spontaneously inflammable phosphuretted hydrogen when heated to redness.

The free acid, HPH_2O_2 , can be obtained from its calcium salt by treatment with the exact quantity of sulphuric acid required to unite with the calcium and form the slightly soluble calcium sulphate. The free acid is a powerful reducing or deoxidising agent,

readily passing by oxidation into phosphorous and ultimately phosphoric acid. The relation of this body to phosphuretted hydrogen on the one side and phosphorous acid on the other is rendered evident by the comparison of the following formulæ—



The existence of an intermediate compound, $\text{PH}_2'(\text{OH})'$, between the two acids is obviously possible.

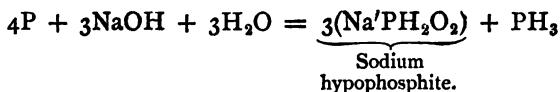
FIG. 109.



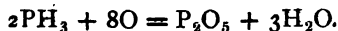
We shall now prepare some phosphuretted hydrogen gas, but we would advise junior readers to defer the experiment until they can make it under skilled guidance, as it is attended with danger unless the following directions are exactly followed :—

Experiment 348.—Pour into a plain untubulated retort of the form shown in fig. 109, and of less than half a liter capacity, sufficient strong solution of

caustic soda to about one-third fill the body of the vessel ; then pass down the neck a few fragments of phosphorus, followed by about one cubic centimeter of *ether*. Now let the long beak of the retort dip under some warm water contained in the large evaporating dish, and apply gentle heat to the retort. The first effect of the heat is to convert the very volatile ether into vapour, and the latter drives out the air from the apparatus, while, as the heat increases, the steam that arises from the solution expels the ether vapour. On boiling the liquid briskly, phosphuretted hydrogen is evolved, but it does not take fire within the retort, as all free oxygen has been expelled in the way pointed out ; it therefore bubbles unchanged through the water in the dish, and as soon as it reaches the air it inflames, and beautiful expanding smoke rings, consisting of phosphorus pentoxide, are formed, for the products of combustion in air or oxygen are the white solid pentoxide and water. The chemical change in progress in the retort is represented by the following equation—



When the gas burns in air its products are—



When it is desired to stop the evolution of gas, withdraw the lamp, but *on no account remove the beak of the retort from the warm water in the capsule* ; then add some boiling water to the contents of the latter.

As the steam in the retort condenses, hot water is slowly drawn in from the capsule and very little gas remains ; if the water in the dish were cold, rapid condensation would occur, and a large quantity of cold water suddenly drawn into the hot retort might cause its destruction with almost explosive violence.

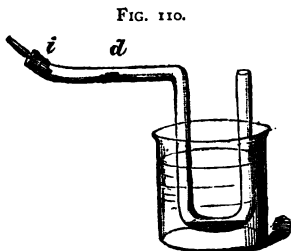
A liquid phosphide, P_2H_4 , and a solid phosphide, P_3H or P_4H_2 , are known ; the former is spontaneously inflammable, and the inflammability of the gas obtained in the above reaction is really due to the presence of a small quantity of the vapour of the liquid, for when the gas is allowed to stand exposed to light it no longer takes fire on mere exposure to air, as the liquid phosphide at first mixed with it is decomposed by light in presence of moisture.

The gaseous hydride is obviously analogous to ammonia in composition, and it further resembles that body in the property of uniting with hydriodic acid to form the compound PH_4I , *phosphonium iodide*, the analogue of NH_4I , ammonium iodide.

We have already found in Experiment 143 that when waxy phosphorus is introduced into a jar of chlorine gas, the phosphorus first melts and then takes fire, obviously owing to rapid chemical union with the chlorine, and produces intensely irritating fumes of a chloride of phosphorus. We shall vary the experiment in the following way.

Experiment 349.—Take a rather wide tube, of the form shown in fig. 110, at *d* place a small quantity of amorphous or red phosphorus, and immerse the bend in a beaker of cold water ; connect the end *i* with an apparatus from which chlorine gas is beir-

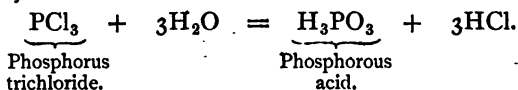
slowly evolved and then dried by making it pass through a calcium chloride tube. Combination takes place without heating the portion of the tube carrying



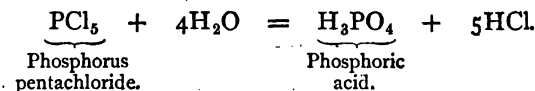
the phosphorus, and a nearly colourless liquid collects at the bend ; this liquid is phosphorus trichloride, PCl_3 , a volatile fuming body. Continue to pass chlorine after the phosphorus has disappeared, and note that the gas is absorbed by the

liquid trichloride and the latter is wholly converted into a yellowish-white powdery substance which can be removed from the tube. This is the highest chloride, PCl_5 , or phosphorus pentachloride.¹

When these chlorides are acted upon by a considerable excess of water they react in the following way—



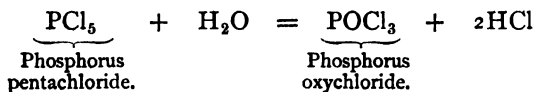
And—



On the other hand, when the pentachloride is

¹ Analogous bromides of phosphorus are known and a tri-iodide, prepared in Experiment 170, as well as an iodide whose formula is P_2I_4 .

mixed with about one-twelfth of its weight of water, or even exposed to moist air, it forms a new liquid body, phosphorus oxychloride, thus—



There are, then, the two simple chlorides of phosphorus and the above oxychloride, but some chemists were disposed to view the solid chloride, PCl_5 , as a compound of the trichloride with a molecule of chlorine, PCl_3Cl_2 , because the body is easily decomposed into these products, and the specific gravity of its vapour is that of a mixture of the kind referred to and not that of a pentachloride. On this view it was not absolutely necessary to regard phosphorus as a pentad, but only as a triad element. This question has, however, been recently set at rest by Professor Thorpe, of Leeds, who has discovered a gaseous pentafluoride of phosphorus, which, unlike its chlorine analogue, is decomposed with great difficulty, and has a specific gravity of 63 ($\text{H} = 1$) ; consequently its molecular weight is 126, which accords with the formula PF_5 .

The specific gravities of several of these volatile phosphorus compounds in the gaseous state are given in the following table, from which it appears that the weight of phosphorus found in one centigram-molecule of each is 31 c.grs. ; therefore the atomic weight of the element cannot be greater than 31 ($\text{H} = 1$),

although the specific gravity of its own vapour would indicate the higher value 62 (see page 261) :—

Compound	Weight of molecule (H = 2)	Weight of P in molecule
Phosphorus trihydride .	34·0	31·0
„ trichloride .	137·5	31·0
„ oxychloride .	153·5	31·0
„ fluoride . .	126·3	31·0

Therefore phosphorus is certainly a pentad element, like nitrogen, and forms compounds which have some analogues among those of the latter. Thus we have the analogous oxides P_2O_5 and N_2O_5 , P_2O_3 and N_2O_3 , the acids HPO_3 and HNO_3 , and the hydrides PH_3 and NH_3 .

Phosphorus and nitrogen are, in fact, closely related members of a family of pentad elements, which includes at least three others, viz., arsenic, antimony and vanadium ; but the latter occupy a pseudo-metallic position, and serve in some degree to connect the group of non-metals with that of true metals, and on this view of their relations we can most conveniently deal with them in Part III.

Poisonous Action—Phosphorus and some of its compounds are powerful poisons, though their precise mode of action is very doubtful. The free element especially is capable of destroying human life when taken in even small quantities ; thus Taylor quotes a case in which a woman, aged 52, took only six centigrams (less than one grain) of phosphorus, in divided doses during four days, and

she died in three days after the last dose. The symptoms are an acrid burning sensation in the throat, garlic odour of the breath, intense thirst, abdominal pain and vomiting. Convulsions are sometimes observed before death. The matters vomited are usually luminous in the dark, and can be tested for free phosphorus as in Experiment 328.¹ Red phosphorus is not known to be poisonous, probably owing to its insolubility and general inertness, and we have already seen that it does not give rise to the chronic form of phosphorus-poisoning caused by the inhalation of vapour, and attended by necrosis of the lower jaw-bone.²

In the treatment of cases of phosphorus-poisoning the use of oily or fatty bodies should be carefully avoided, as they tend, by dissolving the element, to increase its activity. Emetics and mucilaginous drinks containing magnesia are the most appropriate general means to be employed, as the former aid the elimination of any unabsorbed poison, and the magnesia neutralises any acids of phosphorus that may result from slow oxidation of the element. Turpentine and pyrogallic acid have alike been recommended as antidotes, but the value of either is doubt-

¹ If a considerable interval elapses before examination of vomited matter, &c., all traces of free phosphorus may disappear, owing to oxidation.

² The alkaline salts of orthophosphoric acid are not poisonous, but Gamgee has recently made the interesting observation that similar salts of pyro- and metaphosphoric acids are poisonous. These observations will be again referred to when we point out the connection that exists between chemical constitution and physiological activity.

ful, save that turpentine may prove a useful stimulant ; on the other hand, it is open to the same objection as oily or fatty matter—namely, that it is a good solvent for waxy phosphorus, and may therefore help to diffuse it through the system rather than to counteract its effects.

APPENDIX.

SYSTEMATIC TESTING FOR ONE OF THE COMMON ACID RADICLES.

WITH the aid of the Tables given below the student can identify any of the common acids presented to him, or any of their ordinary salts. If the *free acid* be given, it must be *nearly* neutralised with pure NaOH or NH_4OH ; if a *salt of the acid*, it is merely necessary to dissolve a portion in water, and apply the liquid tests in the order given below; but if insoluble in water it is to be dealt with as directed at page 285. All the common acid radicles are divisible into *four groups*, or families, according to their behaviour with two tests—namely, *barium nitrate* and *silver nitrate*, which are termed group reagents.

In order to distinguish the group to which the acid radicle belongs, add first to the neutral liquid $\text{Ba}''(\text{NO}_3)_2$ solution. *A precipitate appears*; then add to the turbid liquid a few drops of moderately strong hydrochloric acid.

a. The precipitate does not dissolve, in which case a member of GROUP I. is indicated, for the radicles of this group agree in forming barium salts, which are insoluble in hydrochloric acid as well as in water,

b. The precipitate dissolves in HCl, in which case a member of GROUP II. is indicated, as their barium salts are insoluble in water, but soluble in the free acid.

Should $\text{Ba}(\text{NO}_3)_2$ fail to cause a precipitate in the neutral solution, Groups I. and II. of acid radicles are absent; then add to a fresh quantity of the liquid to be tested some solution of $\text{Ag}'\text{NO}_3$ —*a precipitate is formed*, pointing to the presence of a radicle of GROUP III., whose members are characterised by forming insoluble silver salts.

The acid radicles forming GROUP IV. do not precipitate from neutral solutions with either $\text{Ba}''(\text{NO}_3)_2$ or $\text{Ag}'\text{NO}_3$.

[NOTE.—The appearances observed on the application of the group tests must be carefully noted and compared with the statements made in the Table under the head of 'Group reaction.']

To distinguish the particular radicle, having found the group, proceed as follows:—Pour a few drops of strong sulphuric acid into a test-tube, and add to the acid a small quantity of the *solid*¹ salt of the radicle, and apply gentle heat. Note accurately what occurs, and compare your observations with the statements in the Table under the head of ' H_2SO_4 treatment.' The effects are generally so characteristic that the particular radicle is directly indicated, but the conclusion drawn must in all cases be tested by appeal to the *confirmatory reactions* given in the third column. These tests are in all cases to be applied to fresh solutions. All the tests not described will be found in detail in the body of the work.

It is found desirable to include in the Table certain

¹ If a solution only is given, or the liquid resulting after a free acid is neutralised, the solution must be evaporated to dryness in a porcelain capsule, and the solid residue then added to the strong sulphuric acid.

acids of common occurrence, whose preparation and properties will be dealt with in Part IV.—viz., oxalic and acetic acids, but the special reactions of these bodies are given in foot-notes.

When a salt is presented for examination which is *insoluble* in water, the analyst must rely on the information he can obtain by the careful treatment of the solid with strong sulphuric acid, as he is obviously precluded from the employment of the group tests, which latter can rarely be used except in neutral liquids. In cases where the H_2SO_4 treatment does not afford definite results, it is necessary to fuse the body with about three times its weight of dry sodium carbonate in a little dish made of a piece of stout platinum foil. When cold, the fused mass is digested with water and the liquid filtered. The clear solution, which contains the sodium salt of the acid, is now just neutralised with pure nitric acid, and the liquid tested as already directed. The metallic radicle of the insoluble salt is usually left on the filter in the form of a carbonate insoluble in water.

When this treatment is applied to barium sulphate, for example, sodium sulphate is dissolved out from the fused mass and barium carbonate is left.

GROUP I.

Group reagents— $\text{Ba}(\text{NO}_3)_2$ followed by HCl. The precipitate is *not dissolved*.

Group reaction.

White p. of BaSO_4 , insoluble in dilute HCl and other acids.White p. of BaSiF_6 , insoluble in HCl. H_2SO_4 treatment.

No result.

Acid fumes evolved, which etch glass, and yield gelatinous silica when a moistened glass rod is held in the gas.

SALTS indicated.

A SULPHATE.—Confirm by AgNO_3 , which gives a white crystalline precipitate of Ag_2SO_4 in *strong* solution.A SILICO-FLUORIDE.—Confirm by testing solution of the salt with KNO_3 . See p. 123.

GROUP II.

Group reagents— $\text{Ba}(\text{NO}_3)_2$ followed by HCl. The precipitate first formed *dissolves*.

Group reaction.

White p. of BaCO_3 , soluble with effervescence in dilute HCl.White p. of BaSO_3 , soluble in dilute HCl, SO_2 evolved, having a suffocating odour.White p. of BaC_2O_4 , soluble in HCl without change. (*P.* not formed if neutral Am. salts are present in large quantity.)White p., $\text{Ba}''\text{F}_2$, soluble in dilute HCl. H_2SO_4 treatment. CO_2 evolved with effervescence. SO_2 evolved with effervescence. Suffocating smell.Gas evolved, is a mixture of CO_2 and CO . The latter burns at mouth of tube with blue flame. See p. 172.

Acid vapour produced, which etches glass and colours Brazil-wood paper yellow.

SALTS indicated.

A CARBONATE.—Confirm by testing gas evolved with lime-water. See p. 155.

A SULPHITE.—Confirm by I bleaching test. See p. 234.

AN OXALATE.—Confirm by CaCl_2 and Acetic acid test.¹A FLUORIDE.—Heated with SiO_2 and H_2SO_4 , affords SiF_4 , which is detected by clouding a moistened glass rod held in the mouth of the tube. See p. 121.

White p. of Ba_3SiO_4 , decomposed by HCl , gelatinous silica separating.	No gas is evolved, but silica separates.	A SILICATE.—Confirm by heating with CaF_2 and H_2SO_4 , when SiF_4 is evolved.
White p. of $\text{Ba}''(\text{BO}_3)_2$, soluble in HCl . If solution be very strong, H_3BO_3 crystallises out after some time. (<i>P.</i> not formed if Am. salts are present.)	No evident change.	A PHOSPHATE or a BORATE.—To distinguish, add to a <i>fresh solution</i> of the substance in water a few drops of AgNO_3 .
White p. of $\text{Ba}''(\text{PO}_4)_2$. Soluble in HCl .		A <i>yellow</i> precipitate is formed if
		A PHOSPHATE. ² Confirm with magnesia mixture. See p. 270.
		A <i>white or brownish</i> precipitate is formed if
		A BORATE. Confirm with turneric-paper test, and flame test. See p. 255.

GROUP III.

Group reagent— AgNO_3 solution.	
SALT ¹ indicated.	
Group reaction.	H_2SO_4 treatment.
White curdy p. of AgCl , soluble in NH_4OH , insoluble in HNO_3 (p. discoloured by light).	Pungent acid gas, fuming in contact with air.
	A CHLORIDE.—Confirm by MnO_2 and H_2SO_4 test; the Cl evolved bleaches moist litmus-paper. See p. 72.

¹ This consists in adding to the solution CaCl_2 , followed by sufficient NH_4OH to render the solution alkaline. If the p. formed under these conditions consists of $\text{Ca}''\text{C}_2\text{O}_4$, it will not dissolve when a considerable excess of acetic acid is added, because calcium oxalate is insoluble in that acid.

² Orthophosphate.

GROUP III. (continued),
Group reagent— AgNO_3 solution.

Group reaction.	H_2SO_4 treatment.	SALTS indicated.
Yellowish-white AgBr , insoluble in HNO_3 (dilute), and soluble with difficulty in NH_4OH .	Brownish-red vapour of Br .	A BROMIDE.—Confirm by Cl water and starch test. See p. 107.
Yellowish-white AgI , insoluble in HNO_3 (dilute), and nearly insoluble in NH_4OH .	Beautiful violet vapour of I .	AN IODIDE.—Confirm by Cl water and starch test; or by HgCl_2 or $\text{Pb}(\text{NO}_3)_2$. See pp. 92 and 99.
White p. of AgCN , soluble in excess of cyanide; with difficulty in NH_4OH , and insoluble in HNO_3 (dilute).	HCN and CO evolved; the latter burns with blue flame at mouth of tube.	A CYANIDE.—Confirm by odour on acidulating with a dilute acid; and by Prussian blue test. ¹ See p. 199.
Whitish precipitate of $\text{Ag}_3\text{Fe}(\text{CN})_6$.	Similar to last, chiefly CO .	A FERROCYANIDE.—Confirm by addition of Fe_2Cl_6 —a deep blue precipitate forms at once. See p. 200.
Reddish-brown p. of $\text{Ag}_3\text{Fe}(\text{CN})_6$.	Ditto.	A +ERRICYANIDE.—Confirm by testing with FeSO_4 solution—a deep blue precipitate forms at once. A brown colouration only is produced with Fe_2Cl_6 . See p. 202.
Black p. of Ag_2S .	H_2S evolved. Smell of rotten eggs.	A SULPHIDE.—Confirm by lead-paper test for gas evolved; and by nitro-prusside of sodium test in a fresh solution. See p. 224.
White p. of Ag_2SO_3 ; becomes black on heating. Ag_2S separating. Excess of thio-sulphate easily dissolves p.	SO_2 evolved. Separates as a yellow mass at the same time.	A THIO-SULPHATE.—Confirm by I bleaching test, and by action of a dilute acid. See pp. 249 and 246.

White p.	Yellow gas evolved, chiefly Cl. Test gas with moist litmus-paper. Brown nitrous fumes.	A HYPOCHLORITE. — Confirm by bleaching test with litmus or red wool, and a dilute acid. See p. 81.
White p. of AgNO_3 in strong solutions.		A NITRITE. — Confirm by KI and starch, followed by acetic acid. See p. 34.

GROUP IV.

Radicles not precipitated by $\text{Ba}(\text{NO}_3)_2$, or by AgNO_3 .²

Treat a *very small* crystal³ of the salt with H_2SO_4 .

A NITRATE. — Confirm by FeSO_4 , adding H_2SO_4 . See pp. 26 and 29.

A CHLORATE. — Confirm by observing effect of heat on the solid—O is evolved, and by indigo test. See p. 86.

AN ACETATE. — Confirm by Fe_2Cl_6 test.⁴

H_2SO_4 treatment.

Gives somewhat brown acid fumes, increased by addition of a little Cu.

⌈ Gives a deep yellow *exsiccative* gas. (A very small quantity of the salt should be used.)

Acid vapour, colourless, but smelling of vinegar.

¹ The odour resembles that of bitter almonds, but great care must be taken to avoid inhalation of much HCN (prussic acid), as it is a *deadly poison*. The Prussian blue test is thus applied :—Add to the solution suspected to contain a cyanide a few drops of FeSO_4 solution, and enough NaOH to render the liquid strongly alkaline; gently warm the mixture, and then add HCl in excess, when a beautiful blue colour will be developed if a cyanide were originally present. (For the explanation of this test, see p. 199 under CYANOGEN.)

² If the solution be very strong, an acetate will give a crystalline p.

³ If a chlorate, dangerous spitting might occur with a large quantity of salt.

⁴ Conducted thus :—Add to the solution some Fe_2Cl_6 containing as little free acid as possible; in presence of an acetate the liquid assumes a reddish-brown colour, and on boiling for some time a precipitate forms, while the odour of vinegar is developed. (For particulars of test see Part IV., under ACETIC ACID.)

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